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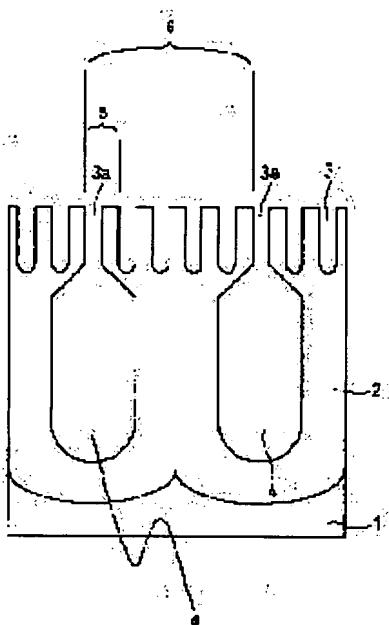
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## (54) POROUS LAYER AND DEVICE, AND ITS MANUFACTURING METHOD



### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous layer having pores composed of a nanostructure, simply controlling the pore density at low cost, and capable of enlarging the area of the pore control and to provide its manufacturing method.

SOLUTION: This porous layer comprises two different pore structures of a first pore group 3 and a second pore group 4 and the first pore group 3 and the second pore group 4 have continuity. In manufacturing the porous structure, a multistage anodic oxidation method is used. Practically, a formation voltage for the anodic oxidation is varied.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the device equipped with the porous layer which has the pore by which consistency control was carried out, and this porous layer, and its manufacture approach.

#### [0002]

[Description of the Prior Art] The nano structure which has the fine structure attracts attention increasingly greatly from unique physical properties being shown electrically and optically. As for the nano structure which has such the fine structure, the application to the various fields to a vacuum micro device, a magnetic device, a luminescence device, a photograph nick device, the quantum effectiveness device, a chemical sensor, magnetic memory, etc. is expected. The alumina oxide film on anode is known for many years as the nano structure which has the fine structure. An alumina oxide film on anode can form the nano structure in self-organization, and ultra-fine processing technology, such as photolithography, electron beam lithography, and X-ray lithography, can say it as the advantageous nano structure industrially at an unnecessary point.

[0003] According to the anodic oxidation technique known from the former, an alumina oxide film on anode is formed in self-organization by anodizing an aluminum plate in acidic solutions, such as a sulfuric acid and oxalic acid. As shown in drawing 12, the alumina oxide film on anode 2 formed on the aluminum substrate 1 has much pores 3 whose diameters are about 5-200nm, and has the structure which this pore 3 arranged regularly. The array structure where such regularity is excellent originates in the alumina oxide film on anode 2 being formed by the cellular structure 25. Such the cellular structure 25 is easily controlled by anodic oxidation conditions, such as applied voltage.

[0004] In recent years, the technique which controls the pore of an alumina oxide film on anode to a precision was indicated by JP,10-121292,A. According to JP,10-121292,A, by being stuck to the aluminum substrate which anodizes the substrate which equipped the front face with two or more projections by pressure, a hollow is formed in an aluminum substrate front face, and this hollow is anodized as an origin. Thus, the formed pore is controlled by spacing of the hollow of the substrate stuck by pressure, and the array by the precision, and has a big merit at the point whose homogeneity of the roundness of pore, a pole diameter, and spacing can improve.

#### [0005]

[Problem(s) to be Solved by the Invention] However, the porosity nature anodic oxidation alumina film indicated by JP,10-121292,A had the technical problem that spacing of pore and an array were uncontrollable by the large area. Moreover, the technique indicated by JP,10-121292,A needed to form beforehand in the mother substrate (mould) the pole diameter by

which the device design was carried out, and the heights which have spacing, and had the technical problem that ultra-fine processing technology was needed for this mould formation. This invention has the pore which is made in order to solve the technical problem of the above-mentioned conventional technique, and consists of nano structure, controls a pore consistency to simplicity and low cost, and aims at offering the device equipped with the porous layer which enabled large area-ization of pore control, and this porous layer, and its manufacture approach. [0006]

[Means for Solving the Problem] In order to attain the above-mentioned object, the porous layer by the invention in this application The 1st pore group which is the porous layer which consists of two or more pores which have nano structure preferably fundamentally, has opening on a front face, and carries out termination in a certain depth, The 1st pore group at least is characterized by having the 2nd pore group from which an aperture differs succeeding said part and depth direction of a pore group of the 1st.

[0007] That is, he is trying to offer a porous layer with the effective pore density structure controlled by the porous layer by the invention in this application by making the 2nd pore group in which it culls out at intervals of a request of the 1st pore group which consists of two or more pores which have nano structure, and an aperture differs from this pore to the pore this operated on a curtailed schedule continue. In the porous layer of the invention in this application, it has the different cellular structure from the 1st pore group and the 2nd pore group preferably, and when the cellular structures differ, the 1st pore group and the 2nd pore group from which configurations, such as a pole diameter, a pore consistency (pore pitch), and pore die length, differ are formed.

[0008] In one gestalt of the porous layer of the invention in this application, the aperture of said 2nd pore group is made larger than the aperture of said 1st pore group. Preferably In there, the gestalt with which said 2nd pore group follows said 1st pore group is made into the gestalt which the pore of two or more 2nd pore groups follows to the pore of the 1st one pore group. Moreover, it is made for said 2nd pore group to have opening on another front face of said front face of said porous layer in one gestalt of the porous layer of the invention in this application.

[0009] The manufacture approach by this invention which manufactures the above-mentioned porous layer is characterized by including the process which forms the 2nd pore group which anodizes on the 1st process which anodizes an anodic oxidation base and forms the 1st pore group fundamentally, and different conditions from said 1st process, and follows a part of 1st pore group. formation voltage [ in / in formation voltage / in / in there, said different conditions are the formation voltage in anodic oxidation preferably, and / said 2nd process / said 1st process ] -- it considers as an integral multiple mostly.

[0010] It explains more concretely. If the porous layer by the invention in this application and its manufacture approach are classified into two, they can do things. First, the 1st porous layer and its manufacture approach are explained. Here, let a substrate outside (the 1st front face exposed spatially substantially) and the 2nd pore group be the substrate insides (the 2nd front face which contacts a substrate substantially) for the 1st pore group. The 1st pore group has the detailed cellular structure of extent which forms the nano structure preferably. The cellular structure which forms the 2nd pore group is larger than the cellular structure which forms the 1st pore group. Therefore, the pore of the 2nd pore group is larger than the pole diameter of the pore of the 1st pore group, and a pore pitch is also large (a pore consistency is small). As shown in drawing 2 explained later, the porous layer later explained as 1st concrete configuration has the configuration which the pore 3 of the 1st pore group which has the nano structure is operated on

a curtailed schedule, and the pore 4 of the 2nd pore group connects with pore 3a of the 1st pore group operated on a curtailed schedule.

[0011] The manufacture approach of the above-mentioned porous layer is characterized by using a multistage story anode oxidation method (here, only a two-step anode oxidation method being explained as simplest approach). In there, formation voltage for forming the 2nd pore group is made larger than the formation voltage for forming the 1st pore group. If formation voltage which forms the V1 and 2nd pore group for the formation voltage which forms the 1st pore group is set to V2, while the ratio of the cell size of the 1st pore group and the cell size of the 2nd pore group is set to V1/V2, the pore of the 2nd pore group will be formed for every [ V2 of the pore of the 1st pore group/] V1. for example, it is V1=30V and V2=150V -- then, cell size [ of the 1st pore group ]: -- it is set to cell size =1:5 of the 2nd pore group, and the pore of the 2nd pore group is formed every five of the pores of the 1st pore group. At this time, the ratio of the pore consistency of the 2nd pore group and the pore consistency of the 1st pore group is set to 1:25, by using for a device the pore penetrated from the 1st front face of a porous layer to the 2nd front face, can operate on a curtailed schedule 1/25 of the pores formed in the 1st front-face side, and becomes controllable [ a substantial pore consistency ]. Offer of the porous layer which has a pore consistency according to a device design is attained from the above thing by controlling the formation voltage which forms the 1st pore group, and the formation voltage which forms the 2nd pore group.

[0012] Next, the 2nd porous layer and its manufacture approach are explained. This porous layer is completely contrary to the configuration of the above-mentioned porous layer, and the cellular structure which forms the 1st pore group is larger than the cellular structure which forms the 2nd pore group. The cellular structure which forms the 2nd pore group is detailed, and, substantially, consists of the pore aggregates (2nd pore group) which reach from the one pore of the 1st pore group to a substrate. in pore 3a of the 1st pore group which the pore 3 of the 1st pore group which has the nano structure thinned out the 2nd porous layer, and it was carried out as shown in drawing 9 explained later, and was thinned out and carried out, the 2nd pore group 17 which consists of the pore aggregates is formed, and it has in it the configuration which leads pore 3a of the 1st pore group to a substrate.

[0013] The manufacture approach of the above-mentioned porous layer is characterized by using a multistage story anode oxidation method like the manufacture approach of the 1st porous layer. In there, formation voltage for forming the 2nd pore group is made smaller than the formation voltage for forming the 1st pore group. If formation voltage which forms the V1 and 2nd pore group for the formation voltage which forms the 1st pore group is set to V2, the pore which even the substrate film (substrate) operated on a curtailed schedule for every [ V1/] V2 penetrates will be formed. For example, if it is V1=40V and V2=20V, the pore aggregate 17 of the 2nd pore group is formed in two of the pore 3 of the 1st pore group at a rate of one piece like drawing 9 .

[0014] As mentioned above, the porous layer of the invention in this application makes it possible to offer the porous layer equipped with the nano structure by which the pore consistency was controlled, when it consists of two different pore structures, the 1st pore group and the 2nd pore group, and a part of 1st pore group and the 2nd pore group have a continuity. Moreover, while such a porous layer is formed in ease and low cost with the multistage story anodic oxidation method using formation voltage change, offer to a large area device of it is attained.

[0015] Therefore, this invention is equipped with one of the porous layers described above on the electrode again. It has further the electron emission section prepared in said pore of the 1st pore group which follows said 2nd pore group and said 2nd pore group. The electron device

characterized by connecting said electron emission section with said electrode electrically substantially is indicated. Moreover, have the porous layer of a gap to describe above on an electrode, or a publication, and it has further the chemical sensor section prepared in said pore of the 1st pore group which follows said 2nd pore group and said 2nd pore group. The chemical sensor device characterized by connecting said chemical sensor section with said electrode electrically substantially is also indicated. according to this invention -- such a device -- setting -- low -- offer of consistency nano structure is attained and the improvement in a property of these devices of it is attained. in addition, this invention -- setting -- "connecting electrically substantially" -- for example, even if it is connection through a thin insulating material etc., it uses as a thing also containing a connection mode in which migration of a charge on another side from one side and supply are substantially performed by tunneling etc. at the time of actuation.

[0016]

[Embodiment of the Invention] <the 1st operation gestalt> -- in the 1st operation gestalt, by increasing the formation voltage of the 2nd-step anodic oxidation (2nd pore group) explains the manufacture approach of a porous layer of having the pore of the selected (infanticide) pore structure, to the formation voltage of the 1st-step anodic oxidation (1st pore group) using a two-step anode oxidation method. Drawing 1 -3 are the process sectional view showing the manufacture approach of the porous layer of this operation gestalt.

[0017] Drawing 1 shows the process sectional view of the porous layer after the 1st-step (1st pore group) anodic oxidation. Like drawing 1 , the aluminum substrate 1 (99% or more of purity is desirable) was anodized, and the alumina oxide film on anode 2 and the pore group 3 were formed. The aluminum substrate 1 impressed and anodized the electrical potential difference of 40V among 0.3M oxalic acid (temperature: 16 degrees C). Drawing 2 shows the process sectional view of the porous layer after the 2nd-step (2nd pore group) anodic oxidation. The pore 4 of the 2nd pore group which connects with a part of pore 3a formed by the 1st pore group like drawing 2 was formed. Anodic oxidation conditions were 195V among the 0.3M phosphoric acid (temperature: 0 degree C).

[0018] At this time, selectivity (thinning out \*\*\*\*\*) (the pitch 5 of the pore of the 1st pore group / pitch 6 of the pore of the 2nd pore group) K can be expressed as  $K^{**}V1/V2$  using applied-voltage:V1 of the 1st-step (1st pore group) anodic oxidation, and applied-voltage:V2 of the 2nd-step (2nd pore group) anodic oxidation. K is approximated to an integer. In this operation gestalt, it is calculable with  $K=40/195^{**}1/5$ . That is, the pore (pore formed from the pore of the 1st pore group and the pore of the 2nd pore group) which penetrates an aluminum substrate has formed the structure which chooses four of five of the pores formed after the 1st-step anodic oxidation (infanticide). At this time, the pore consistency of the pore which penetrates an aluminum substrate decreased to 1/25 of the pore consistencies of the pore of the 1st pore group (V1/V2) (2). Moreover, a pole diameter and cell size increased by those 5 times (V2/V1) the pore of the 1st pore group.

[0019] As mentioned above, by controlling the applied voltage of the 1st-step (1st pore group) anodic oxidation, and the applied voltage of the 2nd-step (2nd pore group) anodic oxidation The pore of the 2nd pore group was prepared in the pore of the 1st pore group chosen according to the device design (infanticide), and the consistency of the penetration pore penetrated from one front face of an oxide film on anode 2 to another front face became controllable.

[0020] Drawing 3 shows the process sectional view of the porous layer after the current recovery for contacting the 2nd pore 4 and aluminum substrate 1 of a pore group. The micropore 7 of an arborescence formed in the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group like

drawing 3 . By forming such micropore 7, the aluminum substrate 1 and contact of the penetration pore formed from the selected pore 3 of the 1st pore group and the selected pore 4 of the 2nd pore group are attained. such current recovery -- the inside of the 2nd 0.3M phosphoric acid (temperature: 0 degree C), and 195V -- receiving -- applied voltage -- 10 -- it was attained by decreasing every [ V ] (195V->185V->175V-> -- > -- >--). When contact to the aluminum substrate 1 is inadequate, by leaving it in a sulfuric-acid solution for several hours, etching clearance is carried out and it becomes enough contacting the about seven-micropore anodized film 2 (alumina;  $Al_2O_3$ ) to the aluminum substrate 1. Such contact needs to be substantially connected with the aluminum substrate 1 electrically. Although it is desirable that the barrier layer of pore 3 pars basilaris ossis occipitalis is removed thoroughly as for substantial electrical installation, if conductivity is secured, it means that the barrier layer may not be removed thoroughly. That is, when a barrier layer is thin enough, it is because it becomes securable [ the conductivity by tunneling ].

[0021] Drawing 4 (a) - (c) shows the process sectional view of the porous layer which filled up penetration pore with the packing material using the penetration pore formed by drawing 1 - drawing 3 . Such a manufacture approach is applicable to a vacuum micro device, a magnetic device, a luminescence device, a photograph nick device, the quantum effectiveness device, a chemical sensor, magnetic memory, etc. In this operation gestalt, a chemical sensor is explained as an example of representation. Drawing 4 (a) separates the \*\*\*\*\* oxide film on anode 2 for the pore 3 of the 1st pore group on the aluminum substrate 1 formed like drawing 3 , the pore 4 of the 2nd pore group, and the micropore 7 of an arborescence, and shows the process sectional view of the porous layer which formed the electrode material 8 in the aluminum substrate of the 1st pore group, and the front face of an opposite hand.

[0022] The anodized film 2 from the aluminum substrate 1 is separated by one of the approaches of whether etching clearance of the aluminum substrate 1 is carried out, or to carry out the reverse point of the potential at the time of anodic oxidation. An electrode material 8 is formed using a spatter or vacuum deposition. If the thickness of an electrode material 8 has desirable about 0.5-1 micrometer and its thickness is thin, it cannot fully cover oxide-film-on-anode 2 front face, but on the other hand, if thickness is thick, the problem of being hard to form a thin film will produce it.

[0023] Drawing 4 (b) removes the barrier layer of the micropore 7 of the arborescence formed in the aluminum substrate 1 side, and shows the process sectional view of the porous layer which filled up selectively the pore of the 1st pore group linked to the 2nd pore group with the sensing ingredient 10. The barrier layer of the micropore 7 of an arborescence was removed using the rare fluoric acid of about 0.5 - 1% of concentration. Thus, by removing the barrier layer of the micropore 7 of an arborescence, opening 9 will be formed and the pore 3 of the 1st pore group linked to the pore 4 of the 2nd pore group will be spatially exposed selectively. Then, the pore 3 of the 1st pore group exposed spatially is selectively filled up with the sensing ingredient 10 by the electric depositing method, for example, electric plating.

[0024] Drawing 4 (c) shows the process sectional view of the porous layer which exposed to space the head of the sensing ingredient 10 with which the pore 3 of the 1st pore group thinned out and (selection) carried out was filled up. Here, the oxide-film-on-anode part of the 2nd pore group is removed. clearance of an anodized film -- an etching removal method or chemical / mechanical polish (CMP;Chemical Mechanical Polishing) -- law is used. In respect of the ease of manufacture, on the etching method and a concrete target, the wet etching method is desirable, and fluoric acid, a phosphoric acid / hydrochloric-acid mixed acid, a sodium hydroxide, etc. can

be used. A sensing ingredient is filled up into a porous layer with the selectivity (rate of infanticide) decided by the applied voltage of the 1st-step (1st pore group) anodic oxidation, and applied voltage of the 2nd-step (2nd pore group) anodic oxidation by penetration pore like drawing 4 (c). In this operation gestalt, the porous layer with which it filled up every five of the pore of the 1st pore group was formed. Thus, unlike the conventional chemical sensor, the consistency of the nano structure was controlled, and since the chemical sensor using the manufactured nano structure had the configuration in which the sensing ingredients with which the nano structure was filled up were moderately scattered, its sensing property of a chemical sensor improved greatly.

[0025] A <operation gestalt of \*\* 2nd> book operation gestalt explains the manufacture approach of the porous layer at the time of using support substrates, such as a glass substrate and a silicon substrate, using drawing 5 and drawing 6 using the two-step anode oxidation method explained with the 1st operation gestalt. The devices using the porous layer of such a configuration are current and the structure where it is widely used for a device, and can be widely applied to various electron devices, an optical device, etc. In this operation gestalt, an electron device is mentioned as the example of representation, and is explained.

[0026] Drawing 5 (a) shows the process sectional view of the porous layer after the 1st-step (1st pore group) anodic oxidation. As a support substrate 11, a glass substrate, a silicon substrate, etc. are desirable. When using a glass substrate, formation of an electrode material is required on the support substrate 11. The silicon substrate was used in this operation gestalt. On a silicon substrate 11, the aluminum deposition film 12 is formed with a spatter, vacuum deposition, etc. The thickness of the aluminum deposition film 12 has desirable about 2-4 micrometers, and when thickness is thin, pore formation is checked, and when thickness is thick, on the other hand, a production process becomes severe. Moreover, as for the front face of the aluminum deposition film 12, it is indispensable that it is a flat, and it is desirable in a visual inspection that it is a mirror plane.

[0027] Thus, the 1st-step (1st pore group) anodic oxidation was performed on the formed aluminum deposition film 12 like drawing 1. Anodic oxidation conditions were 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:40V. Like drawing 5 (a), while the oxide film on anode 2 formed in the surface part of the aluminum deposition film 12 on a silicon substrate 11, the pore 3 of the 1st pore group formed.

[0028] Drawing 5 (b) shows the process sectional view of the porous layer after the 2nd-step (2nd pore group) anodic oxidation. The pore 4 of the 2nd pore group which connects with a part of pore 3a formed by the 1st pore group like the case of drawing 2 was formed. Anodic oxidation conditions were 0.05M oxalic acid, temperature:16 degree C, and applied-voltage:80V. As shown in drawing 5 (b), the barrier layer 13 exists in the pars basilaris ossis occipitalis (pore pars basilaris ossis occipitalis by the side of a silicon substrate 11) of the pore 4 of the 2nd pore group.

[0029] Drawing 6 (a) shows the process sectional view after removing the barrier layer 13 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group. The barrier layer 13 on a silicon substrate was easily removable by continuing and performing anodic oxidation to drawing 5 (b). Thus, by controlling anodization time amount, the barrier layer 13 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group was removed, and the exposed part 14 of a silicon substrate formed. As shown in drawing 6 (a), the pore which has the exposed part 14 of a silicon substrate 11 can offer now the porous layer which controlled the pore consistency by using the pore which was chosen (infanticide) and chosen in this way (infanticide).

[0030] Drawing 6 (b) shows the process sectional view after filling up with a packing material 15

the pore chosen by drawing 6 (a) (infanticide). The electrochemical deposition, i.e., electroplating, of the approach of filling up the selected (infanticide) pore with a packing material 15 is desirable. Like drawing 6 (b), the pore which the silicon substrate 11 exposed was selectively filled up with the packing material 15 by electroplating, and the pore of the 1st pore group was operated on a curtailed schedule as a result. Thus, the porous layer of the invention in this application could be formed not only an aluminum substrate but on the silicon substrate and the glass substrate, and it has checked that it could carry in various devices, such as an electron device and an optical device.

[0031] A <operation gestalt of \*\* 3rd> book operation gestalt explains the manufacture approach of the porous layer at the time of using the support substrates 11, such as a silicon substrate, like the 2nd operation gestalt using drawing 7. In this operation gestalt, a vacuum micro device is mentioned as the example of representation, and is explained. Especially, the manufacture approach of a carbon nanotube electron source is explained as an example of the manufacture approach of the electron source in which low-battery actuation is possible. However, as an electron source ingredient of the invention in this application, it may not be limited to such a carbon material.

[0032] The process sectional view after drawing 7's (a's) forming pore structure on the support substrate 11 with two-step anodic oxidation method like drawing 6 (a), using the pore structure as mold and forming a carbon nanotube 16 is shown. a carbon nanotube 16 -- CVD (Chemical Vapor Deposition) -- it may be formed by law. As the formation approach of such a carbon nanotube 16, a metal catalyst is arranged in the support substrate outcrop 14 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group, and there is also the approach (see the carbon nanotube formation approach of patent No. 3008852) of forming a carbon nanotube by making this metal catalyst into a growth origin. The carbon nanotube 16 was formed in each of the penetration pore which the pore 3 of the 1st pore group, and the pore 3 of the 1st pore group and the pore 4 of the 2nd pore group connected and formed like drawing 7 (a).

[0033] Drawing 7 (b) shows the process sectional view after exposing the head of the selected (infanticide) pore. Head exposure of the carbon nanotube 16 from an anodized film 2 used the wet etching method. As etching for anodized film 2 clearance, fluoric acid, a phosphoric acid, a sodium hydroxide, a phosphoric acid/hydrochloric acid, etc. are used. If such wet etching is performed, the lift off of the carbon nanotube 16a formed in pores 3 other than the penetration pore which the pore 3 of the 1st pore group and the pore 4 of the 2nd pore group connected and formed like drawing 7 (b) is carried out with etching of an anodized film 2, and only the carbon nanotube 16 formed in penetration pore remains. As a result, the carbon nanotube 16 to form is operated on a curtailed schedule and the consistency of a carbon nanotube 16 decreases.

[0034] However, since a carbon film is covered also not only to the wall of pores 3 and 4 but to oxide-film-on-anode 2 front face in the manufacture approach of the carbon nanotube by the CVD method which uses as mold pore structure explained by drawing 7 (a), it is necessary to remove the carbon film of oxide-film-on-anode 2 front face. The carbon film of oxide-film-on-anode 2 front face is easily removable by oxygen plasma etching which used RIE (Reactive IonEtching). As mentioned above, by using two-step anodic oxidation method, by the consistency of a carbon nanotube decreasing and exposing the head of a carbon nanotube, electric-field concentration was able to be raised and low-battery emission was able to be made possible.

[0035] <the 4th operation gestalt> -- in the 4th operation gestalt, the manufacture approach of the porous layer using another two-step anode oxidation method is explained. A different point from

the 1st operation gestalt manufactures the porous layer which has the pore of the pore structure which chose formation voltage of the 2nd-step anodic oxidation (2nd pore group) by decreasing (infanticide) to the formation voltage of the 1st-step anodic oxidation (1st pore group). Drawing 8 -9 are the process sectional view showing the manufacture approach of the porous layer of this operation gestalt.

[0036] Drawing 8 shows the process sectional view after performing the 1st-step anodic oxidation to the aluminum substrate 1 like drawing 1 . Anodic oxidation conditions were 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:40V. Like drawing 8 , while the oxide film on anode 2 formed on the aluminum substrate 1, the pore 3 of the 1st pore group formed. Drawing 9 shows the process sectional view after performing the 2nd-step anodic oxidation. Anodic oxidation conditions are 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:20V, and the pore (pore aggregate) 17 of the 2nd pore group which thinned out and carried out pore 3a of the 1st pore group formed them.

[0037] At this time, selectivity (rate of infanticide) (pitch 19 of the pore which the pore aggregate of the pitch 18 of the pore of the 1st pore group/the 2nd pore group formed) K Applied voltage of the 1st-step (1st pore group) anodic oxidation: Using V1 and applied-voltage:V2 of the 2nd-step (2nd pore group) anodic oxidation, it becomes  $K^{**}V2/V1$  and is set to one half in this operation gestalt. That is, the pore (pore aggregate) 17 of the 2nd pore group forms [ one ] in two of the pores of the 1st pore group. At this time, the pore consistency of the pore which penetrates an oxide film on anode 2 decreased to one fourth of the pores of the 1st pore group.

[0038] Like the 1st operation gestalt as mentioned above, by controlling the applied voltage of the 1st-step (1st pore group) anodic oxidation, and the applied voltage of the 2nd-step (2nd pore group) anodic oxidation The pore (pore aggregate) of the 2nd pore group was prepared in the pore of the 1st pore group chosen according to the device design (infanticide), and the consistency of the penetration pore penetrated from one front face of an oxide film on anode 2 to another front face became controllable.

[0039] Next, drawing 10 and drawing 11 explain the example of representation for applying the porous layer of such a configuration to a device. Drawing 10 (a) - (c) is an example of representation at the time of using an aluminum substrate (configuration applicable to a chemical sensor), and drawing 11 (a) - (c) is an example of representation at the time of using the support substrates 11, such as a glass substrate and a silicon substrate, (configuration applicable to an electron source).

[0040] To the porous layer shown by drawing 9 , drawing 10 (a) removes the aluminum substrate 1, and shows the process sectional view after forming an electrode 20. The aluminum substrate 1 carried out etching clearance with the mixed acid of a phosphoric acid / nitric acid / acetic acid. The electrode 20 was deposited with a spatter and vacuum deposition. Drawing 10 (b) shows the process sectional view after filling up the pore operated on a curtailed schedule with the sensing ingredient 22 after removing the barrier layer of the pore aggregate 17 of the 2nd pore group. The barrier layer was removed by fluoric acid and formed opening 21 in the pore aggregate 17. Drawing 10 (c) shows the process sectional view after exposing the head of the filled sensing ingredient 22. The anodized film 2 was removed using the wet etching method or the chemical / mechanical grinding method. By removing an oxide film on anode 2, the head of the sensing ingredient 22 with which only the pore of the 1st pore group which the pore aggregate of the 2nd pore group formed was filled up was exposed.

[0041] Next, the application of another device is explained. As the 2nd operation gestalt explained, drawing 11 (a) forms the aluminum deposition film 2 on a silicon substrate 11, gives

the 1st and the 2nd-step anodic oxidation like drawing 8 and drawing 9, and shows the process sectional view after putting a carbon film 16 on the wall of pores 3 and 17 with a CVD method. 2 micrometers of aluminum deposition film 2 were formed by the spatter on the silicon substrate 11. Moreover, the 1st-step anodic oxidation was performed by 40V among 0.3M oxalic acid (temperature: 16 degrees C), and the 2nd-step anodic oxidation was performed by 20V among 0.3M oxalic acid (temperature: 16 degrees C). The carbon film (carbon nanotube) formed 800 degrees C and a propylene (inside of nitrogen 2.5%) by making it circulate for 3 hours among the quartz coil.

[0042] Drawing 11 (b) is the process sectional view after exposing a carbon nanotube 16 to space. By carrying out etching clearance of the anodized film 2 by fluoric acid etc., the head of a carbon nanotube is exposed. Although the exposed carbon nanotube consists of a carbon nanotube 23 formed in the penetration pore which consists of a pore aggregate 17 of the pore 3 of the 1st pore group, and the 2nd pore group, and a carbon nanotube 24 formed in 1st pore group independent pore at this time, since floating of the carbon nanotube 24 is carried out electrically, only a carbon nanotube 23 is activity in device substantially. Therefore, the pore formed by the 1st-step anodization as a result was operated on a curtailed schedule, and the pore consistency (carbon nanotube consistency) was reduced. However, when a problem has a carbon nanotube 24 to a device structure target, it is required to carry out a lift off and to remove the unnecessary carbon nanotube 24 by the over etching of an anodized film 2.

[0043] As mentioned above, by making formation voltage of the 2nd-step anodic oxidation smaller than the formation voltage of the 1st-step anodic oxidation, by operating on a curtailed schedule the pore formed by the 1st-step anodic oxidation, and reducing the consistency of the carbon nanotube electron source formed substantially, electric-field concentration was raised and the electron source in which low-battery emission is possible has been offered using the two-step anode oxidation method.

[0044]

[Effect of the Invention] As mentioned above, the porous layer of the invention in this application can obtain easily the thing of the pore consistency by which the request was controlled, though it is the porous layer which has simple structure, since it is obtained by culling out at intervals of a request of the 1st pore group which has nano structure. Moreover, since the manufacture approach of the porous layer by the invention in this application was based on changing the formation voltage in multistage story anodic oxidation, it enabled formation of a large area porous layer, and became entirely unnecessary [ the expensive manufacturing installation in which micro processing is possible ] simultaneously. Furthermore, the porous layer by the invention in this application offers structure advantageous to the device which has the nano structure of a low consistency, and enabled improvement in a device property of a chemical sensor and an electron source especially.

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## TECHNICAL FIELD

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[Field of the Invention] This invention relates to the device equipped with the porous layer which has the pore by which consistency control was carried out, and this porous layer, and its manufacture approach.

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## PRIOR ART

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[Description of the Prior Art] The nano structure which has the fine structure attracts attention increasingly greatly from unique physical properties being shown electrically and optically. As for the nano structure which has such the fine structure, the application to the various fields to a vacuum micro device, a magnetic device, a luminescence device, a photograph nick device, the quantum effectiveness device, a chemical sensor, magnetic memory, etc. is expected. The alumina oxide film on anode is known for many years as the nano structure which has the fine structure. An alumina oxide film on anode can form the nano structure in self-organization, and ultra-fine processing technology, such as photolithography, electron beam lithography, and X-ray lithography, can say it as the advantageous nano structure industrially at an unnecessary point.

[0003] According to the anodic oxidation technique known from the former, an alumina oxide film on anode is formed in self-organization by anodizing an aluminum plate in acidic solutions, such as a sulfuric acid and oxalic acid. As shown in drawing 12, the alumina oxide film on anode 2 formed on the aluminum substrate 1 has much pores 3 whose diameters are about 5-200nm, and has the structure which this pore 3 arranged regularly. The array structure where such regularity is excellent originates in the alumina oxide film on anode 2 being formed by the cellular structure 25. Such the cellular structure 25 is easily controlled by anodic oxidation conditions, such as applied voltage.

[0004] In recent years, the technique which controls the pore of an alumina oxide film on anode to a precision was indicated by JP,10-121292,A. According to JP,10-121292,A, by being stuck to the aluminum substrate which anodizes the substrate which equipped the front face with two or more projections by pressure, a hollow is formed in an aluminum substrate front face, and this hollow is anodized as an origin. Thus, the formed pore is controlled by spacing of the hollow of the substrate stuck by pressure, and the array by the precision, and has a big merit at the point whose homogeneity of the roundness of pore, a pole diameter, and spacing can improve.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] As mentioned above, the porous layer of the invention in this application can obtain easily the thing of the pore consistency by which the request was controlled, though it is the porous layer which has simple structure, since it is obtained by culling out at intervals of a request of the 1st pore group which has nano structure. Moreover, since the manufacture approach of the porous layer by the invention in this application was based on changing the formation voltage in multistage story anodic oxidation, it enabled formation of a large area porous layer, and became entirely unnecessary [ the expensive manufacturing installation in which micro processing is possible ] simultaneously. Furthermore, the porous layer by the invention in this application offers structure advantageous to the device which has the nano structure of a low consistency, and enabled improvement in a device property of a chemical sensor and an electron source especially.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, the porosity nature anodic oxidation alumina film indicated by JP,10-121292,A had the technical problem that spacing of pore and an array were uncontrollable by the large area. Moreover, the technique indicated by JP,10-121292,A needed to form beforehand in the mother substrate (mould) the pole diameter by

which the device design was carried out, and the heights which have spacing, and had the technical problem that ultra-fine processing technology was needed for this mould formation. This invention has the pore which is made in order to solve the technical problem of the above-mentioned conventional technique, and consists of nano structure, controls a pore consistency to simplicity and low cost, and aims at offering the device equipped with the porous layer which enabled large area-ization of pore control, and this porous layer, and its manufacture approach.

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## MEANS

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[Means for Solving the Problem] In order to attain the above-mentioned object, the porous layer by the invention in this application The 1st pore group which is the porous layer which consists of two or more pores which have nano structure preferably fundamentally, has opening on a front face, and carries out termination in a certain depth, The 1st pore group at least is characterized by having the 2nd pore group from which an aperture differs succeeding said part and depth direction of a pore group of the 1st.

[0007] That is, he is trying to offer a porous layer with the effective pore density structure controlled by the porous layer by the invention in this application by making the 2nd pore group in which it culls out at intervals of a request of the 1st pore group which consists of two or more pores which have nano structure, and an aperture differs from this pore to the pore this operated on a curtailed schedule continue. In the porous layer of the invention in this application, it has the different cellular structure from the 1st pore group and the 2nd pore group preferably, and when the cellular structures differ, the 1st pore group and the 2nd pore group from which configurations, such as a pole diameter, a pore consistency (pore pitch), and pore die length, differ are formed.

[0008] In one gestalt of the porous layer of the invention in this application, the aperture of said 2nd pore group is made larger than the aperture of said 1st pore group. Preferably In there, the gestalt with which said 2nd pore group follows said 1st pore group is made into the gestalt which the pore of two or more 2nd pore groups follows to the pore of the 1st one pore group. Moreover, it is made for said 2nd pore group to have opening on another front face of said front face of said porous layer in one gestalt of the porous layer of the invention in this application.

[0009] The manufacture approach by this invention which manufactures the above-mentioned porous layer is characterized by including the process which forms the 2nd pore group which anodizes on the 1st process which anodizes an anodic oxidation base and forms the 1st pore group fundamentally, and different conditions from said 1st process, and follows a part of 1st pore group. formation voltage [ in / in formation voltage / in / in there, said different conditions are the formation voltage in anodic oxidation preferably, and / said 2nd process / said 1st process ] -- it considers as an integral multiple mostly.

[0010] It explains more concretely. If the porous layer by the invention in this application and its manufacture approach are classified into two, they can do things. First, the 1st porous layer and its manufacture approach are explained. Here, let a substrate outside (the 1st front face exposed spatially substantially) and the 2nd pore group be the substrate insides (the 2nd front face which contacts a substrate substantially) for the 1st pore group. The 1st pore group has the detailed cellular structure of extent which forms the nano structure preferably. The cellular structure which forms the 2nd pore group is larger than the cellular structure which forms the 1st pore group. Therefore, the pore of the 2nd pore group is larger than the pole diameter of the pore of the 1st pore group, and a pore pitch is also large (a pore consistency is small). As shown in

drawing 2 explained later, the porous layer later explained as 1st concrete configuration has the configuration which the pore 3 of the 1st pore group which has the nano structure is operated on a curtailed schedule, and the pore 4 of the 2nd pore group connects with pore 3a of the 1st pore group operated on a curtailed schedule.

[0011] The manufacture approach of the above-mentioned porous layer is characterized by using a multistage story anode oxidation method (here, only a two-step anode oxidation method being explained as simplest approach). In there, formation voltage for forming the 2nd pore group is made larger than the formation voltage for forming the 1st pore group. If formation voltage which forms the V1 and 2nd pore group for the formation voltage which forms the 1st pore group is set to V2, while the ratio of the cell size of the 1st pore group and the cell size of the 2nd pore group is set to V1/V2, the pore of the 2nd pore group will be formed for every [ V2 of the pore of the 1st pore group/] V1. for example, it is V1=30V and V2=150V -- then, cell size [ of the 1st pore group ]: -- it is set to cell size =1:5 of the 2nd pore group, and the pore of the 2nd pore group is formed every five of the pores of the 1st pore group. At this time, the ratio of the pore consistency of the 2nd pore group and the pore consistency of the 1st pore group is set to 1:25, by using for a device the pore penetrated from the 1st front face of a porous layer to the 2nd front face, can operate on a curtailed schedule 1/25 of the pores formed in the 1st front-face side, and becomes controllable [ a substantial pore consistency ]. Offer of the porous layer which has a pore consistency according to a device design is attained from the above thing by controlling the formation voltage which forms the 1st pore group, and the formation voltage which forms the 2nd pore group.

[0012] Next, the 2nd porous layer and its manufacture approach are explained. This porous layer is completely contrary to the configuration of the above-mentioned porous layer, and the cellular structure which forms the 1st pore group is larger than the cellular structure which forms the 2nd pore group. The cellular structure which forms the 2nd pore group is detailed, and, substantially, consists of the pore aggregates (2nd pore group) which reach from the one pore of the 1st pore group to a substrate. in pore 3a of the 1st pore group which the pore 3 of the 1st pore group which has the nano structure thinned out the 2nd porous layer, and it was carried out as shown in drawing 9 explained later, and was thinned out and carried out, the 2nd pore group 17 which consists of the pore aggregates is formed, and it has in it the configuration which leads pore 3a of the 1st pore group to a substrate.

[0013] The manufacture approach of the above-mentioned porous layer is characterized by using a multistage story anode oxidation method like the manufacture approach of the 1st porous layer. In there, formation voltage for forming the 2nd pore group is made smaller than the formation voltage for forming the 1st pore group. If formation voltage which forms the V1 and 2nd pore group for the formation voltage which forms the 1st pore group is set to V2, the pore which even the substrate film (substrate) operated on a curtailed schedule for every [ V1/] V2 penetrates will be formed. For example, if it is V1=40V and V2=20V, the pore aggregate 17 of the 2nd pore group is formed in two of the pore 3 of the 1st pore group at a rate of one piece like drawing 9 .

[0014] As mentioned above, the porous layer of the invention in this application makes it possible to offer the porous layer equipped with the nano structure by which the pore consistency was controlled, when it consists of two different pore structures, the 1st pore group and the 2nd pore group, and a part of 1st pore group and the 2nd pore group have a continuity. Moreover, while such a porous layer is formed in ease and low cost with the multistage story anodic oxidation method using formation voltage change, offer to a large area device of it is attained.

[0015] Therefore, this invention is equipped with one of the porous layers described above on the

electrode again. It has further the electron emission section prepared in said pore of the 1st pore group which follows said 2nd pore group and said 2nd pore group. The electron device characterized by connecting said electron emission section with said electrode electrically substantially is indicated. Moreover, have the porous layer of a gap to describe above on an electrode, or a publication, and it has further the chemical sensor section prepared in said pore of the 1st pore group which follows said 2nd pore group and said 2nd pore group. The chemical sensor device characterized by connecting said chemical sensor section with said electrode electrically substantially is also indicated. according to this invention -- such a device -- setting -- low -- offer of consistency nano structure is attained and the improvement in a property of these devices of it is attained. in addition, this invention -- setting -- "connecting electrically substantially" -- for example, even if it is connection through a thin insulating material etc., it uses as a thing also containing a connection mode in which migration of a charge on another side from one side and supply are substantially performed by tunneling etc. at the time of actuation.

[0016]

[Embodiment of the Invention] <the 1st operation gestalt> -- in the 1st operation gestalt, by increasing the formation voltage of the 2nd-step anodic oxidation (2nd pore group) explains the manufacture approach of a porous layer of having the pore of the selected (infanticide) pore structure, to the formation voltage of the 1st-step anodic oxidation (1st pore group) using a two-step anode oxidation method. Drawing 1 - 3 are the process sectional view showing the manufacture approach of the porous layer of this operation gestalt.

[0017] Drawing 1 shows the process sectional view of the porous layer after the 1st-step (1st pore group) anodic oxidation. Like drawing 1 , the aluminum substrate 1 (99% or more of purity is desirable) was anodized, and the alumina oxide film on anode 2 and the pore group 3 were formed. The aluminum substrate 1 impressed and anodized the electrical potential difference of 40V among 0.3M oxalic acid (temperature: 16 degrees C). Drawing 2 shows the process sectional view of the porous layer after the 2nd-step (2nd pore group) anodic oxidation. The pore 4 of the 2nd pore group which connects with a part of pore 3a formed by the 1st pore group like drawing 2 was formed. Anodic oxidation conditions were 195V among the 0.3M phosphoric acid (temperature: 0 degree C).

[0018] At this time, selectivity (thinning out \*\*\*\*\*) (the pitch 5 of the pore of the 1st pore group / pitch 6 of the pore of the 2nd pore group) K can be expressed as  $K^{**}V1/V2$  using applied-voltage:V1 of the 1st-step (1st pore group) anodic oxidation, and applied-voltage:V2 of the 2nd-step (2nd pore group) anodic oxidation. K is approximated to an integer. In this operation gestalt, it is calculable with  $K=40/195^{**}1/5$ . That is, the pore (pore formed from the pore of the 1st pore group and the pore of the 2nd pore group) which penetrates an aluminum substrate has formed the structure which chooses four of five of the pores formed after the 1st-step anodic oxidation (infanticide). At this time, the pore consistency of the pore which penetrates an aluminum substrate decreased to 1/25 of the pore consistencies of the pore of the 1st pore group (V1/V2) (2). Moreover, a pole diameter and cell size increased by those 5 times (V2/V1) the pore of the 1st pore group.

[0019] As mentioned above, by controlling the applied voltage of the 1st-step (1st pore group) anodic oxidation, and the applied voltage of the 2nd-step (2nd pore group) anodic oxidation The pore of the 2nd pore group was prepared in the pore of the 1st pore group chosen according to the device design (infanticide), and the consistency of the penetration pore penetrated from one front face of an oxide film on anode 2 to another front face became controllable.

[0020] Drawing 3 shows the process sectional view of the porous layer after the current recovery

for contacting the 2nd pore 4 and aluminum substrate 1 of a pore group. The micropore 7 of an arborescence formed in the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group like drawing 3. By forming such micropore 7, the aluminum substrate 1 and contact of the penetration pore formed from the selected pore 3 of the 1st pore group and the selected pore 4 of the 2nd pore group are attained. such current recovery -- the inside of the 2nd 0.3M phosphoric acid (temperature: 0 degree C), and 195V -- receiving -- applied voltage -- 10 -- it was attained by decreasing every [ V ] (195V>185V>175V->-->-->--). When contact to the aluminum substrate 1 is inadequate, by leaving it in a sulfuric-acid solution for several hours, etching clearance is carried out and it becomes enough contacting the about seven-micropore anodized film 2 (alumina; Ar 2O3) to the aluminum substrate 1. Such contact needs to be substantially connected with the aluminum substrate 1 electrically. Although it is desirable that the barrier layer of pore 3 pars basilaris ossis occipitalis is removed thoroughly as for substantial electrical installation, if conductivity is secured, it means that the barrier layer may not be removed thoroughly. That is, when a barrier layer is thin enough, it is because it becomes securable [ the conductivity by tunneling ].

[0021] Drawing 4 (a) - (c) shows the process sectional view of the porous layer which filled up penetration pore with the packing material using the penetration pore formed by drawing 1 - drawing 3. Such a manufacture approach is applicable to a vacuum micro device, a magnetic device, a luminescence device, a photograph nick device, the quantum effectiveness device, a chemical sensor, magnetic memory, etc. In this operation gestalt, a chemical sensor is explained as an example of representation. Drawing 4 (a) separates the \*\*\*\*\* oxide film on anode 2 for the pore 3 of the 1st pore group on the aluminum substrate 1 formed like drawing 3, the pore 4 of the 2nd pore group, and the micropore 7 of an arborescence, and shows the process sectional view of the porous layer which formed the electrode material 8 in the aluminum substrate of the 1st pore group, and the front face of an opposite hand.

[0022] The anodized film 2 from the aluminum substrate 1 is separated by one of the approaches of whether etching clearance of the aluminum substrate 1 is carried out, or to carry out the reverse point of the potential at the time of anodic oxidation. An electrode material 8 is formed using a spatter or vacuum deposition. If the thickness of an electrode material 8 has desirable about 0.5-1 micrometer and its thickness is thin, it cannot fully cover oxide-film-on-anode 2 front face, but on the other hand, if thickness is thick, the problem of being hard to form a thin film will produce it.

[0023] Drawing 4 (b) removes the barrier layer of the micropore 7 of the arborescence formed in the aluminum substrate 1 side, and shows the process sectional view of the porous layer which filled up selectively the pore of the 1st pore group linked to the 2nd pore group with the sensing ingredient 10. The barrier layer of the micropore 7 of an arborescence was removed using the rare fluoric acid of about 0.5 - 1% of concentration. Thus, by removing the barrier layer of the micropore 7 of an arborescence, opening 9 will be formed and the pore 3 of the 1st pore group linked to the pore 4 of the 2nd pore group will be spatially exposed selectively. Then, the pore 3 of the 1st pore group exposed spatially is selectively filled up with the sensing ingredient 10 by the electric depositing method, for example, electric plating.

[0024] Drawing 4 (c) shows the process sectional view of the porous layer which exposed to space the head of the sensing ingredient 10 with which the pore 3 of the 1st pore group thinned out and (selection) carried out was filled up. Here, the oxide-film-on-anode part of the 2nd pore group is removed. clearance of an anodized film -- an etching removal method or chemical / mechanical polish (CMP;Chemical Mechanical Polishing) -- law is used. In respect of the ease of

manufacture, on the etching method and a concrete target, the wet etching method is desirable, and fluoric acid, a phosphoric acid / hydrochloric-acid mixed acid, a sodium hydroxide, etc. can be used. A sensing ingredient is filled up into a porous layer with the selectivity (rate of infanticide) decided by the applied voltage of the 1st-step (1st pore group) anodic oxidation, and applied voltage of the 2nd-step (2nd pore group) anodic oxidation by penetration pore like drawing 4 (c). In this operation gestalt, the porous layer with which it filled up every five of the pore of the 1st pore group was formed. Thus, unlike the conventional chemical sensor, the consistency of the nano structure was controlled, and since the chemical sensor using the manufactured nano structure had the configuration in which the sensing ingredients with which the nano structure was filled up were moderately scattered, its sensing property of a chemical sensor improved greatly.

[0025] A <operation gestalt of \*\* 2nd> book operation gestalt explains the manufacture approach of the porous layer at the time of using support substrates, such as a glass substrate and a silicon substrate, using drawing 5 and drawing 6 using the two-step anode oxidation method explained with the 1st operation gestalt. The devices using the porous layer of such a configuration are current and the structure where it is widely used for a device, and can be widely applied to various electron devices, an optical device, etc. In this operation gestalt, an electron device is mentioned as the example of representation, and is explained.

[0026] Drawing 5 (a) shows the process sectional view of the porous layer after the 1st-step (1st pore group) anodic oxidation. As a support substrate 11, a glass substrate, a silicon substrate, etc. are desirable. When using a glass substrate, formation of an electrode material is required on the support substrate 11. The silicon substrate was used in this operation gestalt. On a silicon substrate 11, the aluminum deposition film 12 is formed with a spatter, vacuum deposition, etc. The thickness of the aluminum deposition film 12 has desirable about 2-4 micrometers, and when thickness is thin, pore formation is checked, and when thickness is thick, on the other hand, a production process becomes severe. Moreover, as for the front face of the aluminum deposition film 12, it is indispensable that it is a flat, and it is desirable in a visual inspection that it is a mirror plane.

[0027] Thus, the 1st-step (1st pore group) anodic oxidation was performed on the formed aluminum deposition film 12 like drawing 1. Anodic oxidation conditions were 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:40V. Like drawing 5 (a), while the oxide film on anode 2 formed in the surface part of the aluminum deposition film 12 on a silicon substrate 11, the pore 3 of the 1st pore group formed.

[0028] Drawing 5 (b) shows the process sectional view of the porous layer after the 2nd-step (2nd pore group) anodic oxidation. The pore 4 of the 2nd pore group which connects with a part of pore 3a formed by the 1st pore group like the case of drawing 2 was formed. Anodic oxidation conditions were 0.05M oxalic acid, temperature:16 degree C, and applied-voltage:80V. As shown in drawing 5 (b), the barrier layer 13 exists in the pars basilaris ossis occipitalis (pore pars basilaris ossis occipitalis by the side of a silicon substrate 11) of the pore 4 of the 2nd pore group.

[0029] Drawing 6 (a) shows the process sectional view after removing the barrier layer 13 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group. The barrier layer 13 on a silicon substrate was easily removable by continuing and performing anodic oxidation to drawing 5 (b). Thus, by controlling anodization time amount, the barrier layer 13 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group was removed, and the exposed part 14 of a silicon substrate formed. As shown in drawing 6 (a), the pore which has the exposed part 14 of a silicon substrate 11 can offer now the porous layer which controlled the pore consistency

by using the pore which was chosen (infanticide) and chosen in this way (infanticide).

[0030] Drawing 6 (b) shows the process sectional view after filling up with a packing material 15 the pore chosen by drawing 6 (a) (infanticide). The electrochemical deposition, i.e., electroplating, of the approach of filling up the selected (infanticide) pore with a packing material 15 is desirable. Like drawing 6 (b), the pore which the silicon substrate 11 exposed was selectively filled up with the packing material 15 by electroplating, and the pore of the 1st pore group was operated on a curtailed schedule as a result. Thus, the porous layer of the invention in this application could be formed not only an aluminum substrate but on the silicon substrate and the glass substrate, and it has checked that it could carry in various devices, such as an electron device and an optical device.

[0031] A <operation gestalt of \*\* 3rd> book operation gestalt explains the manufacture approach of the porous layer at the time of using the support substrates 11, such as a silicon substrate, like the 2nd operation gestalt using drawing 7. In this operation gestalt, a vacuum micro device is mentioned as the example of representation, and is explained. Especially, the manufacture approach of a carbon nanotube electron source is explained as an example of the manufacture approach of the electron source in which low-battery actuation is possible. However, as an electron source ingredient of the invention in this application, it may not be limited to such a carbon material.

[0032] The process sectional view after drawing 7's (a's) forming pore structure on the support substrate 11 with two-step anodic oxidation method like drawing 6 (a), using the pore structure as mold and forming a carbon nanotube 16 is shown. a carbon nanotube 16 -- CVD (Chemical Vapor Deposition) -- it may be formed by law. As the formation approach of such a carbon nanotube 16, a metal catalyst is arranged in the support substrate outcrop 14 of the pars basilaris ossis occipitalis of the pore 4 of the 2nd pore group, and there is also the approach (see the carbon nanotube formation approach of patent No. 3008852) of forming a carbon nanotube by making this metal catalyst into a growth origin. The carbon nanotube 16 was formed in each of the penetration pore which the pore 3 of the 1st pore group, and the pore 3 of the 1st pore group and the pore 4 of the 2nd pore group connected and formed like drawing 7 (a).

[0033] Drawing 7 (b) shows the process sectional view after exposing the head of the selected (infanticide) pore. Head exposure of the carbon nanotube 16 from an anodized film 2 used the wet etching method. As etching for anodized film 2 clearance, fluoric acid, a phosphoric acid, a sodium hydroxide, a phosphoric acid/hydrochloric acid, etc. are used. If such wet etching is performed, the lift off of the carbon nanotube 16a formed in pores 3 other than the penetration pore which the pore 3 of the 1st pore group and the pore 4 of the 2nd pore group connected and formed like drawing 7 (b) is carried out with etching of an anodized film 2, and only the carbon nanotube 16 formed in penetration pore remains. As a result, the carbon nanotube 16 to form is operated on a curtailed schedule and the consistency of a carbon nanotube 16 decreases.

[0034] However, since a carbon film is covered also not only to the wall of pores 3 and 4 but to oxide-film-on-anode 2 front face in the manufacture approach of the carbon nanotube by the CVD method which uses as mold pore structure explained by drawing 7 (a), it is necessary to remove the carbon film of oxide-film-on-anode 2 front face. The carbon film of oxide-film-on-anode 2 front face is easily removable by oxygen plasma etching which used RIE (Reactive IonEtching). As mentioned above, by using two-step anodic oxidation method, by the consistency of a carbon nanotube decreasing and exposing the head of a carbon nanotube, electric-field concentration was able to be raised and low-battery emission was able to be made possible.

[0035] <the 4th operation gestalt> -- in the 4th operation gestalt, the manufacture approach of the porous layer using another two-step anode oxidation method is explained. A different point from the 1st operation gestalt manufactures the porous layer which has the pore of the pore structure which chose formation voltage of the 2nd-step anodic oxidation (2nd pore group) by decreasing (infanticide) to the formation voltage of the 1st-step anodic oxidation (1st pore group). Drawing 8 -9 are the process sectional view showing the manufacture approach of the porous layer of this operation gestalt.

[0036] Drawing 8 shows the process sectional view after performing the 1st-step anodic oxidation to the aluminum substrate 1 like drawing 1 . Anodic oxidation conditions were 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:40V. Like drawing 8 , while the oxide film on anode 2 formed on the aluminum substrate 1, the pore 3 of the 1st pore group formed. Drawing 9 shows the process sectional view after performing the 2nd-step anodic oxidation. Anodic oxidation conditions are 0.3M oxalic acid, temperature:16 degree C, and applied-voltage:20V, and the pore (pore aggregate) 17 of the 2nd pore group which thinned out and carried out pore 3a of the 1st pore group formed them.

[0037] At this time, selectivity (rate of infanticide) (pitch 19 of the pore which the pore aggregate of the pitch 18 of the pore of the 1st pore group/the 2nd pore group formed) K Applied voltage of the 1st-step (1st pore group) anodic oxidation: Using V1 and applied-voltage:V2 of the 2nd-step (2nd pore group) anodic oxidation, it becomes  $K^{**}V2/V1$  and is set to one half in this operation gestalt. That is, the pore (pore aggregate) 17 of the 2nd pore group forms [ one ] in two of the pores of the 1st pore group. At this time, the pore consistency of the pore which penetrates an oxide film on anode 2 decreased to one fourth of the pores of the 1st pore group.

[0038] Like the 1st operation gestalt as mentioned above, by controlling the applied voltage of the 1st-step (1st pore group) anodic oxidation, and the applied voltage of the 2nd-step (2nd pore group) anodic oxidation The pore (pore aggregate) of the 2nd pore group was prepared in the pore of the 1st pore group chosen according to the device design (infanticide), and the consistency of the penetration pore penetrated from one front face of an oxide film on anode 2 to another front face became controllable.

[0039] Next, drawing 10 and drawing 11 explain the example of representation for applying the porous layer of such a configuration to a device. Drawing 10 (a) - (c) is an example of representation at the time of using an aluminum substrate (configuration applicable to a chemical sensor), and drawing 11 (a) - (c) is an example of representation at the time of using the support substrates 11, such as a glass substrate and a silicon substrate, (configuration applicable to an electron source).

[0040] To the porous layer shown by drawing 9 , drawing 10 (a) removes the aluminum substrate 1, and shows the process sectional view after forming an electrode 20. The aluminum substrate 1 carried out etching clearance with the mixed acid of a phosphoric acid / nitric acid / acetic acid. The electrode 20 was deposited with a spatter and vacuum deposition. Drawing 10 (b) shows the process sectional view after filling up the pore operated on a curtailed schedule with the sensing ingredient 22 after removing the barrier layer of the pore aggregate 17 of the 2nd pore group. The barrier layer was removed by fluoric acid and formed opening 21 in the pore aggregate 17. Drawing 10 (c) shows the process sectional view after exposing the head of the filled sensing ingredient 22. The anodized film 2 was removed using the wet etching method or the chemical / mechanical grinding method. By removing an oxide film on anode 2, the head of the sensing ingredient 22 with which only the pore of the 1st pore group which the pore aggregate of the 2nd pore group formed was filled up was exposed.

[0041] Next, the application of another device is explained. As the 2nd operation gestalt explained, drawing 11 (a) forms the aluminum deposition film 2 on a silicon substrate 11, gives the 1st and the 2nd-step anodic oxidation like drawing 8 and drawing 9, and shows the process sectional view after putting a carbon film 16 on the wall of pores 3 and 17 with a CVD method. 2 micrometers of aluminum deposition film 2 were formed by the spatter on the silicon substrate 11. Moreover, the 1st-step anodic oxidation was performed by 40V among 0.3M oxalic acid (temperature: 16 degrees C), and the 2nd-step anodic oxidation was performed by 20V among 0.3M oxalic acid (temperature: 16 degrees C). The carbon film (carbon nanotube) formed 800 degrees C and a propylene (inside of nitrogen 2.5%) by making it circulate for 3 hours among the quartz coil.

[0042] Drawing 11 (b) is the process sectional view after exposing a carbon nanotube 16 to space. By carrying out etching clearance of the anodized film 2 by fluoric acid etc., the head of a carbon nanotube is exposed. Although the exposed carbon nanotube consists of a carbon nanotube 23 formed in the penetration pore which consists of a pore aggregate 17 of the pore 3 of the 1st pore group, and the 2nd pore group, and a carbon nanotube 24 formed in 1st pore group independent pore at this time, since floating of the carbon nanotube 24 is carried out electrically, only a carbon nanotube 23 is activity in device substantially. Therefore, the pore formed by the 1st-step anodization as a result was operated on a curtailed schedule, and the pore consistency (carbon nanotube consistency) was reduced. However, when a problem has a carbon nanotube 24 to a device structure target, it is required to carry out a lift off and to remove the unnecessary carbon nanotube 24 by the over etching of an anodized film 2.

[0043] As mentioned above, by making formation voltage of the 2nd-step anodic oxidation smaller than the formation voltage of the 1st-step anodic oxidation, by operating on a curtailed schedule the pore formed by the 1st-step anodic oxidation, and reducing the consistency of the carbon nanotube electron source formed substantially, electric-field concentration was raised and the electron source in which low-battery emission is possible has been offered using the two-step anode oxidation method.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] The process sectional view of the porous layer in the 1st operation gestalt is shown.

[Drawing 2] The process sectional view of the porous layer in the 1st operation gestalt is shown.

[Drawing 3] The process sectional view of the porous layer in the 1st operation gestalt is shown.

[Drawing 4] The process sectional view of the chemical sensor using the porous layer in the 1st operation gestalt is shown.

[Drawing 5] The process sectional view of the electron device using the porous layer in the 2nd operation gestalt is shown.

[Drawing 6] The process sectional view of the electron device using the porous layer in the 2nd operation gestalt is shown.

[Drawing 7] The process sectional view of a carbon nanotube electron source using the porous layer in the 3rd operation gestalt is shown.

[Drawing 8] The process sectional view of the porous layer in the 4th operation gestalt is shown.

[Drawing 9] The process sectional view of the porous layer in the 4th operation gestalt is shown.

[Drawing 10] The process sectional view of the chemical sensor using the porous layer in the 4th operation gestalt is shown.

[Drawing 11] The process sectional view of a carbon nanotube electron source using the porous layer in the 4th operation gestalt is shown.

[Drawing 12] The perspective view of an alumina oxide film on anode is shown.

[Description of Notations]

- 1 Aluminum Substrate
- 2 Oxide Film on Anode
- 3 3a Pore of the 1st pore group
- 4 Pore of 2nd Pore Group
- 5 Pitch of Pore of 1st Pore Group
- 6 Pitch of Pore of 2nd Pore Group
- 7 Micropore
- 8 Electrode
- 9 Opening of Pore Pars Basilaris Ossis Occipitalis of 2nd Pore Group
- 10 Sensing Ingredient
- 11 Support Substrate
- 12 Aluminum Deposition Film
- 13 Barrier Layer of Pore of 2nd Pore Group
- 14 Contact Section of Pore Pars Basilaris Ossis Occipitalis of 2nd Pore Group
- 15 Packing Material
- 16 Carbon Nanotube
- 17 Pore Aggregate
- 18 Pitch of Pore of 1st Pore Group
- 19 Pitch of Pore of 1st Pore Group Which Pore Aggregate of 2nd Pore Group Formed
- 20 Electrode
- 21 Opening of Pore Aggregate Pars Basilaris Ossis Occipitalis
- 22 Sensing Ingredient
- 23 Carbon Nanotube in contact with Substrate Layer
- 24 Carbon Nanotube Which Carried Out Floating

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## CLAIMS

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[Claim(s)]

[Claim 1] The 1st pore group at least is a porous layer characterized by having the 2nd pore group from which an aperture differs succeeding the part and the depth direction of the 1st pore group which is the porous layer which consists of two or more pores, has opening on the 1st front face, and carries out termination in a certain depth, and said 1st pore group.

[Claim 2] The porous layer according to claim 1 to which the aperture of said 2nd pore group is characterized by being larger than the aperture of said 1st pore group.

[Claim 3] The porous layer according to claim 2 characterized by the gestalt with which said 2nd pore group follows said 1st pore group being a gestalt which the pore of two or more 2nd pore groups follows to the pore of the 1st one pore group.

[Claim 4] There is no claim 1 characterized by having opening on the 2nd front face said whose 2nd pore group is another front face of said 1st front face of said porous layer, and it is the porous layer of a publication 3 either.

[Claim 5] The electron device characterized by having further the electron emission section prepared at the pore of the claim 1 thru/or 1st [ said ] pore group which is equipped with the

porous layer of a publication 4 either, and follows said 2nd pore group and said 2nd pore group, and connecting said electron emission section with said electrode electrically substantially on an electrode.

[Claim 6] The chemical sensor device characterized by having further the chemical sensor section prepared at the pore of the claim 1 thru/or 1st [ said ] pore group which is equipped with the porous layer of a publication 4 either, and follows said 2nd pore group and said 2nd pore group, and connecting said chemical sensor section with said electrode electrically substantially on an electrode.

[Claim 7] The manufacture approach of the porous layer characterized by including the process which forms the 2nd pore group which anodizes on the 1st process which anodizes an anodic oxidation base and forms the 1st pore group, and different conditions from said 1st process, and follows a part of 1st pore group.

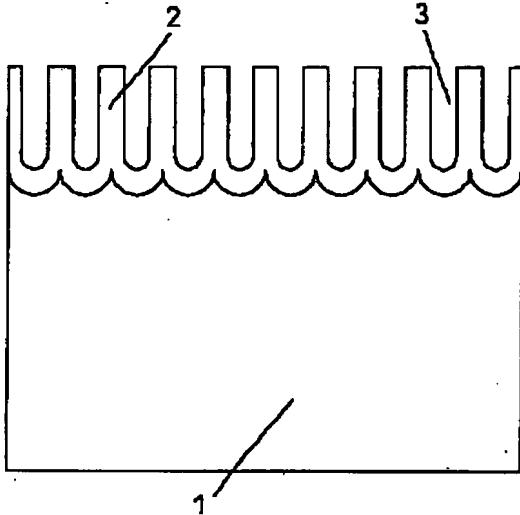
[Claim 8] The manufacture approach of a porous layer that it is the manufacture approach of a porous layer according to claim 7, said different conditions are the formation voltage in anodic oxidation, and formation voltage in said 2nd process is characterized by being [ of the formation voltage in said 1st process ] an integral multiple mostly.

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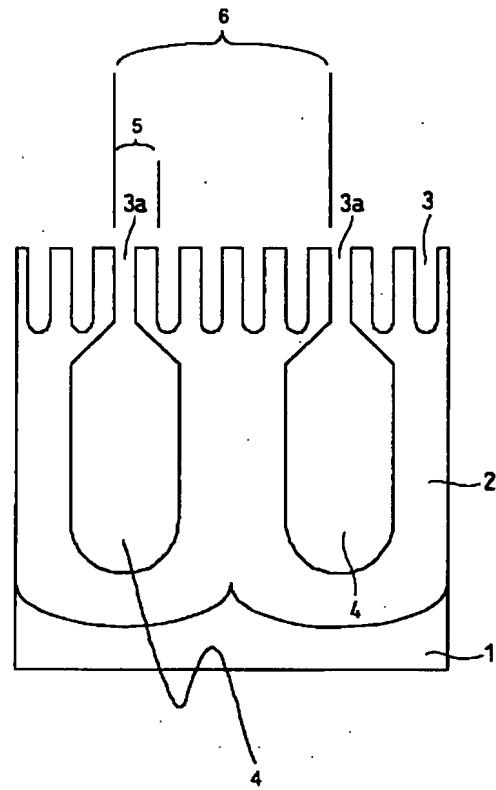
## DRAWINGS

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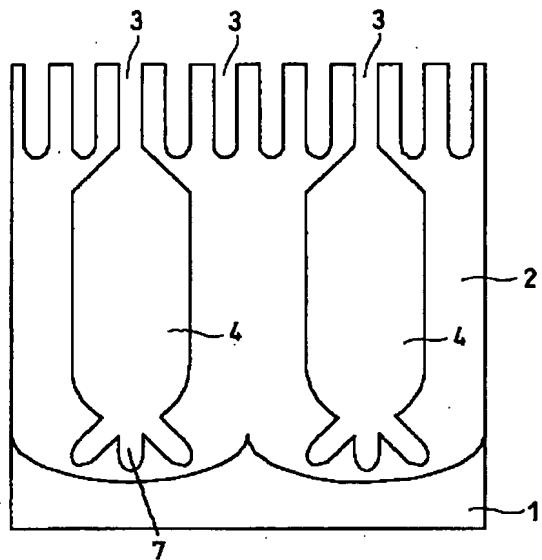
[Drawing 1]



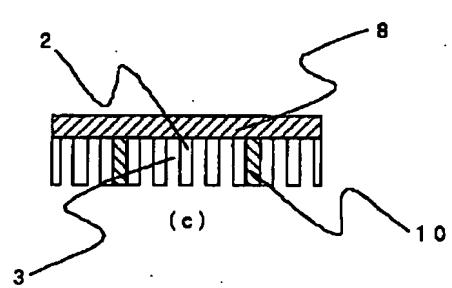
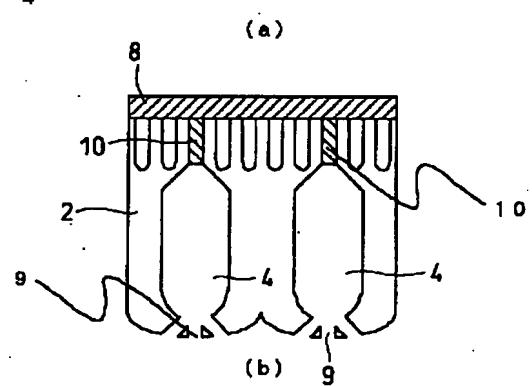
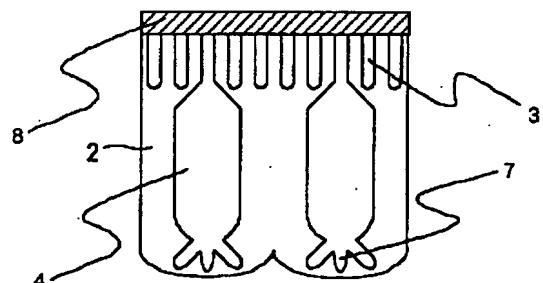
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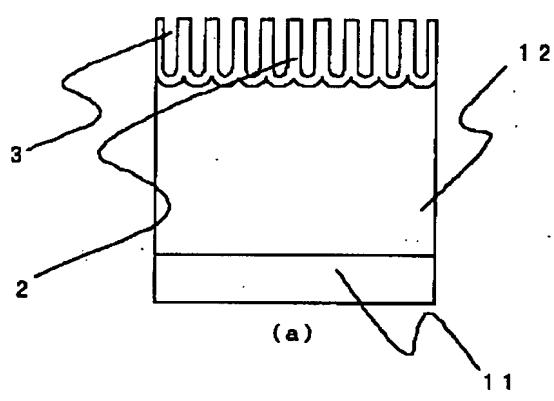
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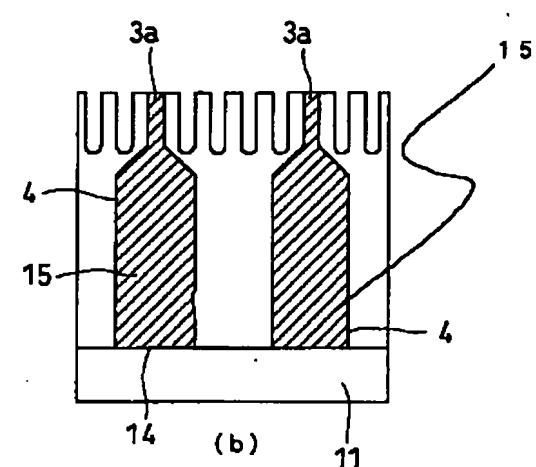
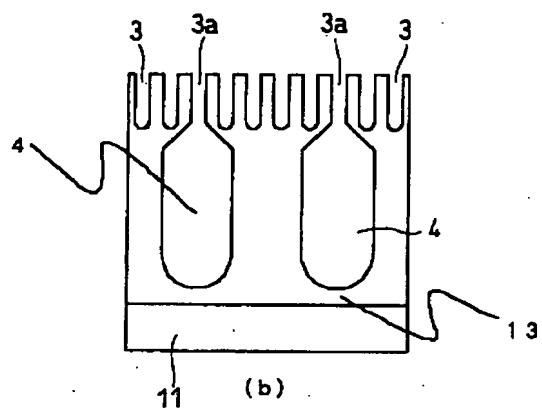
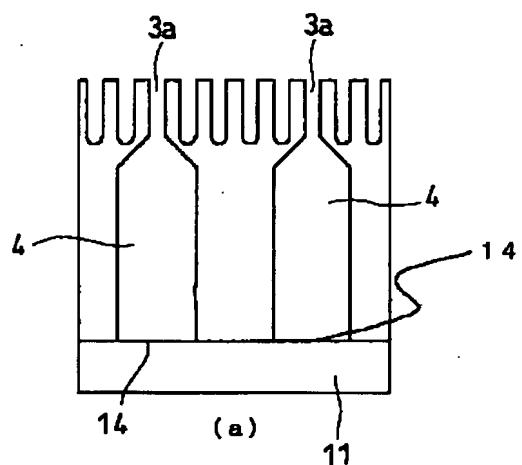
[Drawing 4]



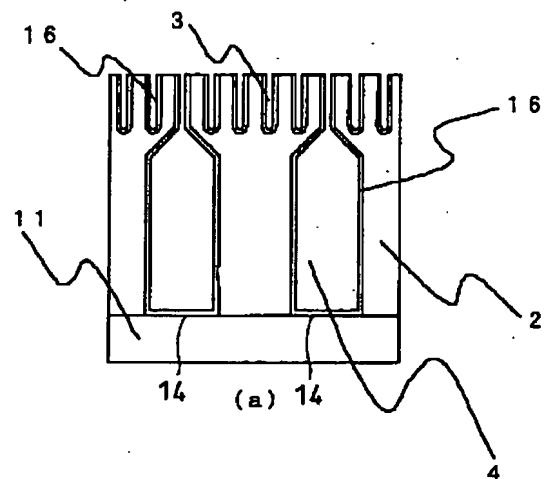
[Drawing 5]



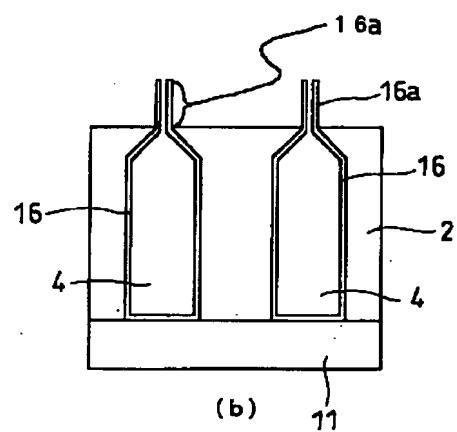
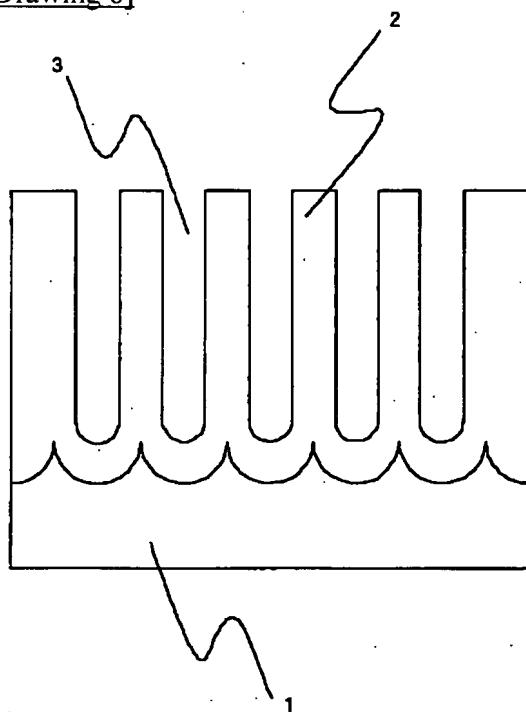
[Drawing 6]



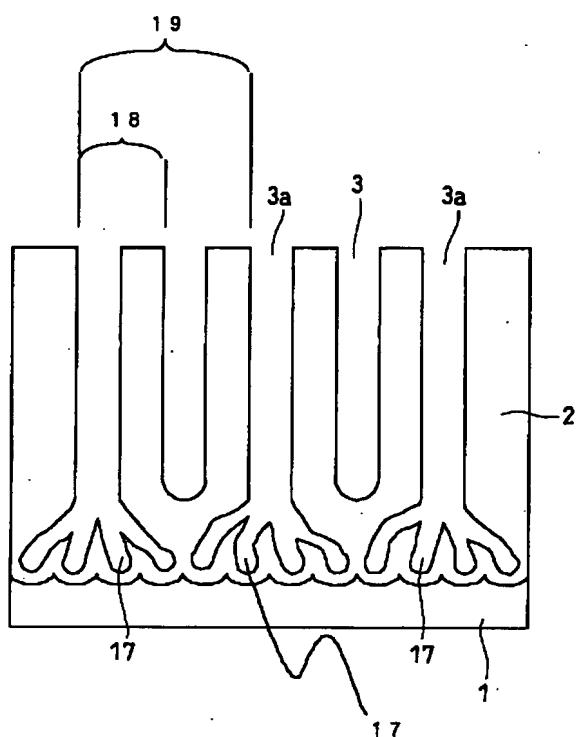
[Drawing 7]



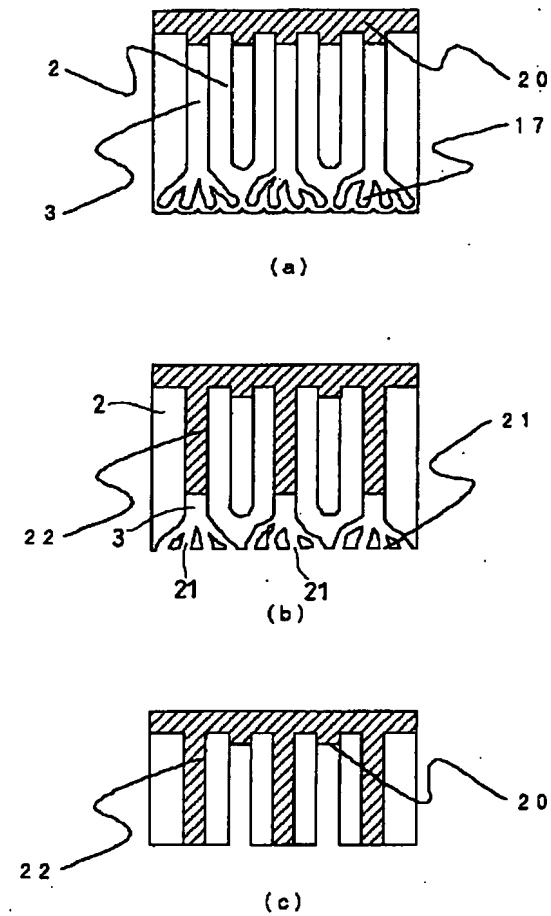
[Drawing 8]



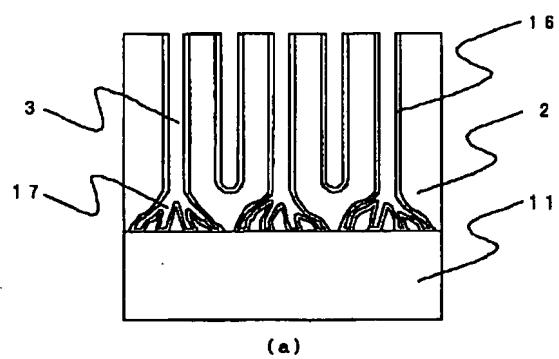
[Drawing 9]



[Drawing 10]

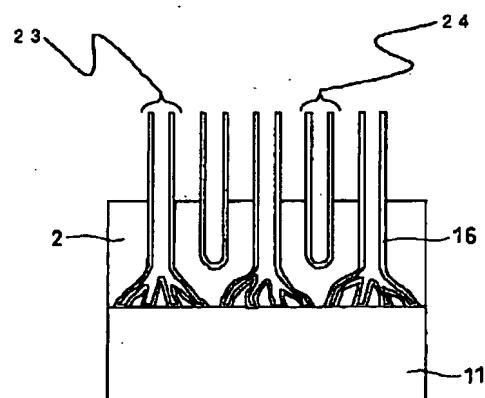
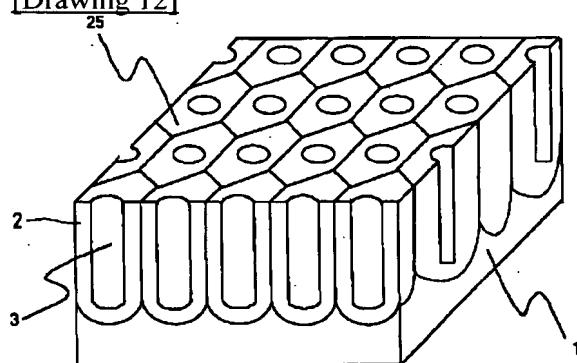


[Drawing 11]



(a)

[Drawing 12]



(b)

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[Translation done.]

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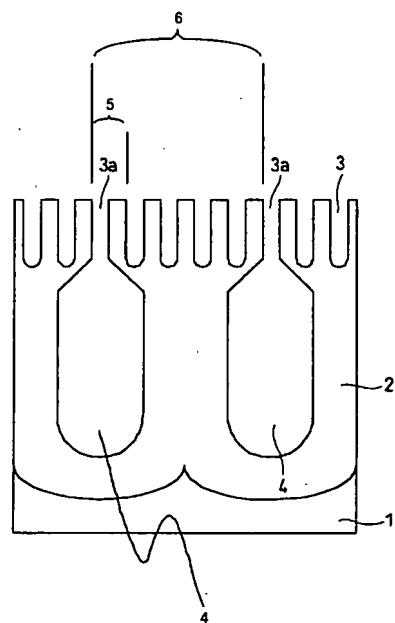
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(54)【発明の名称】 多孔質層及びデバイス、並びにその製造方法

(57)【要約】

【課題】 ナノ構造からなる細孔を有し、細孔密度を簡便、且つ、低成本に制御し、細孔制御の大面積化を可能にした多孔質層及びその製造方法を提供する。

【解決手段】 多孔質層は第1の細孔群3、第2の細孔群4の2つの異なる細孔構造から構成され、一部の第1の細孔群3と第2の細孔群4とが連続性を有する。多孔質層の製造に当たっては、多段階陽極酸化法を用いる。具体的には、陽極酸化するための化成電圧を変化させる。



## 【特許請求の範囲】

【請求項1】複数の細孔から構成される多孔質層であって、第1の表面に開口を有し、ある深さで終端する第1の細孔群と、前記第1の細孔群の一部と深さ方向に連続し、少なくとも第1の細孔群とは孔径の異なる第2の細孔群とを備えたことを特徴とする多孔質層。

【請求項2】前記第2の細孔群の孔径が前記第1の細孔群の孔径よりも大きいことを特徴とする請求項1記載の多孔質層。

【請求項3】前記第2の細孔群が前記第1の細孔群に連続する形態が、一つの第1の細孔群の細孔に対して、複数の第2の細孔群の細孔が連続する形態であることを特徴とする請求項2記載の多孔質層。

【請求項4】前記第2の細孔群が前記多孔質層の前記第1の表面のもう一方の表面である第2の表面に開口を有することを特徴とする請求項1ないし3いずれか記載の多孔質層。

【請求項5】電極上に請求項1ないし4いずれか記載の多孔質層を備え、前記第2の細孔群と前記第2の細孔群と連続する前記第1の細孔群の細孔に設けられた電子放出部を更に備え、前記電子放出部が前記電極と実質的に電気的に接続されていることを特徴とする電子デバイス。

【請求項6】電極上に請求項1ないし4いずれか記載の多孔質層を備え、前記第2の細孔群と前記第2の細孔群と連続する前記第1の細孔群の細孔に設けられた化学センサー部を更に備え、前記化学センサー部が前記電極と実質的に電気的に接続されていることを特徴とする化学センサーデバイス。

【請求項7】陽極酸化基体を陽極酸化して第1の細孔群を形成する第1の工程と、前記第1の工程とは異なる条件で陽極酸化して第1の細孔群の一部と連続する第2の細孔群を形成する工程とを含むことを特徴とする多孔質層の製造方法。

【請求項8】請求項7に記載の多孔質層の製造方法であって、前記異なる条件が陽極酸化における化成電圧であり、前記第2の工程における化成電圧が前記第1の工程における化成電圧のほぼ整数倍であることを特徴とする多孔質層の製造方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、密度制御された細孔を有する多孔質層と該多孔質層を備えたデバイス及びその製造方法に関する。

## 【0002】

【従来の技術】微細構造を有するナノ構造体が、電気的、光学的に特異な物性を示すことから、大きく注目されるようになってきている。このような微細構造を有するナノ構造体は、真空マイクロデバイス、磁気デバイス、発光デバイス、フォトニックデバイス、量子効果デ

バイス、化学センサー、磁気メモリ等への種々の分野への応用が期待されている。微細構造を有するナノ構造体として、アルミナ陽極酸化膜が古くから知られている。アルミナ陽極酸化膜は、ナノ構造体を自己組織的に形成することが可能であり、フォトリソグラフィー、電子線露光、X線露光等の微細加工技術が不要である点で、工業的に有利なナノ構造体と言える。

【0003】従来から知られている陽極酸化技術によれば、アルミナ陽極酸化膜は、アルミニウム板を硫酸、シ

10 ュウ酸等の酸性溶液中で陽極酸化することにより自己組織的に形成する。図12に示すように、アルミニウム基板1上に形成されたアルミナ陽極酸化膜2は、直径が5～200nm程度の細孔3を多数有し、この細孔3が規則正しく配列した構造をもっている。このような規則性が優れる配列構造は、アルミナ陽極酸化膜2がセル構造25で形成されることに由来するものである。このようなセル構造25は、印加電圧等の陽極酸化条件で容易に制御される。

【0004】近年、アルミナ陽極酸化膜の細孔を精密に20 制御する技術が特開平10-121292号公報に開示された。特開平10-121292号公報によれば、複数の突起を表面に備えた基板を陽極酸化するアルミニウム基板に圧着することにより、アルミニウム基板表面に窪みを形成し、この窪みを起点として陽極酸化する。このようにして形成された細孔は、圧着する基板の窪みの間隔、配列で精密に制御され、細孔の真円度、細孔径及び間隔の均一性が向上できる点で大きなメリットがある。

## 【0005】

30 【発明が解決しようとする課題】しかしながら、特開平10-121292号公報に開示される多孔質性陽極酸化アルミナ膜は、細孔の間隔、配列を大面積で制御することができないという課題があった。また、特開平10-121292号公報に開示される技術は、デバイス設計された細孔径、間隔を有する凸部を予め、母基板（モールド）に形成する必要があり、このモールド形成に微細加工技術を必要とするという課題があった。本発明は、上記従来技術の課題を解決するためになされたものであり、ナノ構造からなる細孔を有し、細孔密度を簡便、且つ、低コストに制御し、細孔制御の大面積化を可能にした多孔質層と該多孔質層を備えたデバイス及びその製造方法を提供することを目的とする。

## 【0006】

【課題を解決するための手段】上記目的を達成するため、本願発明による多孔質層は、基本的に、好ましくはナノ構造を有する複数の細孔から構成される多孔質層であって、表面に開口を有し、ある深さで終端する第1の細孔群と、前記第1の細孔群の一部と深さ方向に連続し、少なくとも第1の細孔群とは孔径の異なる第2の細孔群とを備えたことを特徴とする。

【0007】すなわち、本願発明による多孔質層では、ナノ構造を有する複数の細孔から構成される第1の細孔群を所望の間隔で間引きして、該間引きされた細孔に対して該細孔とは孔径の異なる第2の細孔群を連続させることにより、制御された有効細孔密度構造を持つ多孔質層を提供するようにしている。好ましくは、本願発明の多孔質層において、第1の細孔群と第2の細孔群とは異なるセル構造を有しており、セル構造が異なることにより、細孔径、細孔密度（細孔ピッチ）、細孔長さ等の形状が異なる第1の細孔群と第2の細孔群が形成される。

【0008】本願発明の多孔質層の一形態において、前記第2の細孔群の孔径が前記第1の細孔群の孔径よりも大きいものとされ、好ましくは、そこにおいて、前記第2の細孔群が前記第1の細孔群に連続する形態が、一つの第1の細孔群の細孔に対して、複数の第2の細孔群の細孔が連続する形態とされる。また、本願発明の多孔質層の一形態において、前記第2の細孔群が前記多孔質層の前記表面のもう一方の表面に開口を有するようにされる。

【0009】上記の多孔質層を製造する本発明による製造方法は、基本的に、陽極酸化基体を陽極酸化して第1の細孔群を形成する第1の工程と、前記第1の工程とは異なる条件で陽極酸化して第1の細孔群の一部と連続する第2の細孔群を形成する工程とを含むことを特徴とする。そこにおいて、好ましくは、前記異なる条件が陽極酸化における化成電圧であり、前記第2の工程における化成電圧が前記第1の工程における化成電圧のほぼ整数倍とされる。

【0010】より具体的に説明する。本願発明による多孔質層及びその製造方法は、2つに分類することができる。まず、第1の多孔質層及びその製造方法を説明する。ここで、第1の細孔群を基板外側（実質的には、空間的に露出する第1の表面）、第2の細孔群を基板内側（実質的には、基板と接触する第2の表面）とする。第1の細孔群は、好ましくはナノ構造体を形成する程度の微細セル構造を有する。第2の細孔群を形成するセル構造は、第1の細孔群を形成するセル構造よりも大きい。従って、第2の細孔群の細孔は、第1の細孔群の細孔の細孔径よりも大きく、細孔ピッチも大きい（細孔密度が小さい）。後に説明する図2に示すように、第1の具体的な構成として後に説明する多孔質層は、ナノ構造体を有する第1の細孔群の細孔3が間引きされ、間引きされた第1の細孔群の細孔3aに第2の細孔群の細孔4が連結する構成を有する。

【0011】上記の多孔質層の製造方法は、多段階陽極酸化法（ここでは、2段階陽極酸化法のみを最も単純な方法として説明する）を用いることを特徴とする。そこにおいて、第2の細孔群を形成するための化成電圧を第1の細孔群を形成するための化成電圧よりも大きくする。第1の細孔群を形成する化成電圧をV1、第2の細

孔群を形成する化成電圧をV2とすると、第1の細孔群のセルサイズと第2の細孔群のセルサイズの比はV1/V2となると共に、第1の細孔群の細孔のV2/V1毎に第2の細孔群の細孔が形成される。例えば、V1=30V、V2=150Vであるとすれば、第1の細孔群のセルサイズ：第2の細孔群のセルサイズ=1:5となり、第1の細孔群の細孔の5つ毎に第2の細孔群の細孔が形成される。この時、第2の細孔群の細孔密度と第1の細孔群の細孔密度との比は1:25となり、多孔質層の第1の表面から第2の表面まで貫通する細孔をデバイスに用いることにより、第1の表面側に形成した細孔の1/25を間引きでき、実質的な細孔密度の制御が可能となる。以上のことから、第1の細孔群を形成する化成電圧と第2の細孔群を形成する化成電圧とを制御することにより、デバイス設計に応じた細孔密度を有する多孔質層が提供可能となる。

【0012】次に、第2の多孔質層及びその製造方法を説明する。この多孔質層は、上記した多孔質層の構成と全く逆であり、第1の細孔群を形成するセル構造は、第2の細孔群を形成するセル構造よりも大きい。第2の細孔群を形成するセル構造は微細であり、実質的には、第1の細孔群の一つ細孔から基板へ達する細孔集合体（第2の細孔群）で構成される。後に説明する図9に示すように、第2の多孔質層は、ナノ構造体を有する第1の細孔群の細孔3が間引きされ、間引きされた第1の細孔群の細孔3aには、細孔集合体から構成される第2の細孔群17が設けられ、第1の細孔群の細孔3aを基板へと導く構成を有する。

【0013】上記の多孔質層の製造方法は、第1の多孔質層の製造方法と同様に、多段階陽極酸化法を用いることを特徴とする。そこにおいて、第2の細孔群を形成するための化成電圧は第1の細孔群を形成するための化成電圧よりも小さくされる。第1の細孔群を形成する化成電圧をV1、第2の細孔群を形成する化成電圧をV2とすると、V1/V2毎に間引きされた、下地膜（基板）まで貫通する細孔が形成される。例えば、V1=40V、V2=20Vであるとすれば、図9のように、第2の細孔群の細孔集合体17は、第1の細孔群の細孔3の2個に1個の割合で形成される。

【0014】以上のように、本願発明の多孔質層は、第1の細孔群、第2の細孔群の2つの異なる細孔構造から構成され、第1の細孔群の一部と第2の細孔群とが連続性を有することにより、細孔密度が制御されたナノ構造を備えた多孔質層を提供することを可能にする。また、このような多孔質層は、化成電圧変化を利用した多段階陽極酸化法で容易、且つ、低コストに形成されると共に、大面積なデバイスに提供可能となる。

【0015】従って、本発明は、また、電極上に上記したいずれかの多孔質層を備え、前記第2の細孔群と前記第2の細孔群と連続する前記第1の細孔群の細孔に設け

られた電子放出部を更に備え、前記電子放出部が前記電極と実質的に電気的に接続されていることを特徴とする電子デバイスを開示し、また、電極上に上記したいずれか記載の多孔質層を備え、前記第2の細孔群と前記第2の細孔群と連続する前記第1の細孔群の細孔に設けられた化学センサー部を更に備え、前記化学センサー部が前記電極と実質的に電気的に接続されていることを特徴とする化学センサーデバイスをも開示する。本発明によれば、そのようなデバイスにおいて、低密度なナノ構造が提供可能となり、それらデバイスの特性向上が可能となる。なお、本発明において「実質的に電気的に接続」とは、例えば、薄い絶縁物等を介した接続であっても、動作時に、トンネリング等により一方から他方への電荷の移動、供給が実質的に行われるような接続様式をも含むものとして用いている。

#### 【0016】

【発明の実施の形態】<第1の実施形態>第1の実施形態に於いては、2段階陽極酸化法を用い、第1段階目の陽極酸化（第1の細孔群）の化成電圧に対して、第2段階目の陽極酸化（第2の細孔群）の化成電圧を増加することにより、選択（間引き）した細孔構造の細孔を有する多孔質層の製造方法を説明する。図1～3は、本実施形態の多孔質層の製造方法を示す工程断面図である。

【0017】図1は、第1段階目（第1の細孔群）の陽極酸化後の多孔質層の工程断面図を示す。図1のように、アルミニウム基板1（純度は99%以上が好ましい）を陽極酸化し、アルミナ陽極酸化膜2と細孔群3を形成した。アルミニウム基板1は、0.3M硫酸中（温度：16°C）、40Vの電圧を印加し、陽極酸化した。図2は、第2段階目（第2の細孔群）の陽極酸化後の多孔質層の工程断面図を示す。図2のように、第1の細孔群で形成された一部の細孔3aと接続する第2の細孔群の細孔4を形成した。陽極酸化条件は、0.3M硫酸中（温度：0°C）、195Vであった。

【0018】この時、選択率（間引き率）K（第1の細孔群の細孔のピッチ5／第2の細孔群の細孔のピッチ6）は、第1段階目（第1の細孔群）の陽極酸化の印加電圧：V1、第2段階目（第2の細孔群）の陽極酸化の印加電圧：V2を用い、

$$K = V1/V2$$

と表わすことができる。Kは整数に近似される。本実施形態に於いては、

$$K = 40/195 = 1/5$$

と計算できる。即ち、アルミニウム基板を貫通する細孔（第1の細孔群の細孔と第2の細孔群の細孔から形成される細孔）は、第1段階目の陽極酸化後に形成した細孔の5つの内、4つを選択（間引き）する構造が形成できた。この時、アルミニウム基板を貫通する細孔の細孔密度は、第1の細孔群の細孔の細孔密度の1/25（(V1/V2)^2）に減少した。また、細孔径及びセルサイ

ズは、第1の細孔群の細孔のそれらの5倍（V2/V1）に増加した。

【0019】以上のように、第1段階目（第1の細孔群）の陽極酸化の印加電圧、第2段階目（第2の細孔群）の陽極酸化の印加電圧を制御することにより、デバイス設計に応じて選択（間引き）された第1の細孔群の細孔に第2の細孔群の細孔が設けられ、陽極酸化膜2の一方の表面からもう一方の表面へ貫通する貫通細孔の密度が制御可能になった。

10 【0020】図3は、第2の細孔群の細孔4とアルミニウム基板1をコンタクトさせるための電流回復処理後の多孔質層の工程断面図を示す。図3のように、第2の細孔群の細孔4の底部に樹状の微細孔7が形成した。このような微細孔7を形成することにより、選択された第1の細孔群の細孔3と第2の細孔群の細孔4から形成される貫通細孔は、アルミニウム基板1とコンタクト可能になる。このような電流回復処理は、第2の0.3M硫酸中（温度：0°C）、195Vに対して、印加電圧を10Vずつ減少（195V→185V→175V→…）することにより、達成された。アルミニウム基板1とのコンタクトが不十分である場合、硫酸溶液中で数時間放置することにより、微細孔7近傍の陽極酸化膜2（アルミナ； $Al_2O_3$ ）がエッチング除去され、アルミニウム基板1に対するコンタクトが十分となる。このようなコンタクトは、実質的にアルミニウム基板1と電気的に接続されている必要がある。実質的な電気的接続とは、細孔3底部のバリア層が完全に除去されていることが好ましいが、導電性が確保されればバリア層が完全に除去されていなくても構わないことを意味する。即ち、

20 30 バリア層が十分に薄い場合、トンネリングによる導電性の確保が可能となるためである。

【0021】図4(a)～(c)は、図1～図3で形成した貫通細孔を用い、貫通細孔に充填材料を充填した多孔質層の工程断面図を示す。このような製造方法は、真空マイクロデバイス、磁気デバイス、発光デバイス、フォトニックデバイス、量子効果デバイス、化学センサー、磁気メモリ等に応用可能である。本実施形態に於いては、化学センサーを代表例として説明する。図4(a)は、図3のように形成したアルミニウム基板1上の第1の細孔群の細孔3、第2の細孔群の細孔4、樹状の微細孔7を設けた陽極酸化膜2を分離し、第1の細孔群のアルミニウム基板と反対側の表面に電極材料8を設けた多孔質層の工程断面図を示す。

【0022】アルミニウム基板1からの陽極酸化膜2は、アルミニウム基板1をエッチング除去するか、または、陽極酸化時の電位を逆点するかのどちらかの方法により、分離する。電極材料8は、スパッタ法、または、蒸着法を用い、形成する。電極材料8の膜厚は、0.5～1μm程度が好ましく、膜厚が薄いと陽極酸化膜2表面を十分に覆えず、一方、膜厚が厚いと薄膜を形成し難

いという問題が生じる。

【0023】図4 (b) は、アルミニウム基板1側に形成した樹状の微細孔7のバリア層を除去し、第2の細孔群に接続した第1の細孔群の細孔に選択的にセンシング材料10を充填した多孔質層の工程断面図を示す。樹状の微細孔7のバリア層は、0.5~1%程度の濃度の希フッ酸を用いて除去した。このように樹状の微細孔7のバリア層を除去することにより、開口部9が形成され、第2の細孔群の細孔4に接続した第1の細孔群の細孔3が選択的に空間的に露出することになる。引き続き、電気的な堆積法、例えば、電気メッキ法により、空間的に露出した第1の細孔群の細孔3に選択的に、センシング材料10が充填される。

【0024】図4 (c) は、間引き(選択)された第1の細孔群の細孔3に充填されたセンシング材料10の先端を空間に露出した多孔質層の工程断面図を示す。ここでは、第2の細孔群の陽極酸化膜部分を除去する。陽極酸化膜の除去は、エッチング除去法、または、化学的・機械的研磨(CMP: Chemical Mechanical Polishing)法を用いる。製造の容易さの点では、エッチング法、具体的にはウエットエッチング法が好ましく、フッ酸、リン酸/塩酸混酸、水酸化ナトリウム等を用いることができる。図4 (c) のように、多孔質層は、第1段階目(第1の細孔群)の陽極酸化の印加電圧、第2段階目(第2の細孔群)の陽極酸化の印加電圧で決まる選択率(間引き率)でセンシング材料を貫通細孔に充填される。本実施形態に於いては、第1の細孔群の細孔の5個毎に充填された多孔質層が形成された。このようにして製造されたナノ構造体を用いた化学センサーは、従来の化学センサーと異なり、ナノ構造体の密度が制御され、ナノ構造体に充填されたセンシング材料が適度に散在した構成を有するため、化学センサーのセンシング特性が大きく向上した。

【0025】<第2の実施形態>本実施形態では、第1の実施形態で説明した2段階陽極酸化法を用い、ガラス基板、シリコン基板等の支持基板を用いた場合の多孔質層の製造方法を、図5及び図6を用いて説明する。このような構成の多孔質層を用いたデバイスは、現在、広くデバイスに用いられる構造であり、種々の電子デバイス、光デバイス等に広く応用可能である。本実施形態に於いては、電子デバイスを代表例に挙げて説明する。

【0026】図5 (a) は、第1段階目(第1の細孔群)の陽極酸化後の多孔質層の工程断面図を示す。支持基板11としては、ガラス基板、シリコン基板等が好ましい。ガラス基板を用いる場合、支持基板11上に電極材料の形成が必要である。本実施形態に於いては、シリコン基板を用いた。シリコン基板11上に、スパッタ法、蒸着法等でアルミニウム堆積膜12を形成する。アルミニウム堆積膜12の膜厚は、2~4 μm程度が好ましく、膜厚が薄い場合は、細孔形成が阻害され、一方、

膜厚が厚い場合は、製造工程が厳しくなる。また、アルミニウム堆積膜12の表面はフラットであることが不可欠であり、目視検査に於いては、鏡面であることが好ましい。

【0027】このようにして形成されたアルミニウム堆積膜12に、図1と同様に、第1段階目(第1の細孔群)の陽極酸化を行った。陽極酸化条件は、0.3Mシュウ酸、温度:16°C、印加電圧:40Vであった。図5 (a) のように、シリコン基板11上のアルミニウム堆積膜12の表面部分に陽極酸化膜2が形成すると共に、第1の細孔群の細孔3が形成した。

【0028】図5 (b) は、第2段階目(第2の細孔群)の陽極酸化後の多孔質層の工程断面図を示す。図2の場合と同様に、第1の細孔群で形成された一部の細孔3aと接続する第2の細孔群の細孔4を形成した。陽極酸化条件は、0.05Mシュウ酸、温度:16°C、印加電圧:80Vであった。図5 (b) に示すように、第2の細孔群の細孔4の底部(シリコン基板11側の細孔底部)にはバリア層13が存在する。

【0029】図6 (a) は、第2の細孔群の細孔4の底部のバリア層13を除去した後の工程断面図を示す。シリコン基板上のバリア層13は、陽極酸化を図5 (b) に引き続き行うことにより、容易に除去可能であった。このように、陽極酸化時間を制御することにより、第2の細孔群の細孔4の底部のバリア層13が除去され、シリコン基板の露出部分14が形成した。図6 (a) に示すように、シリコン基板11の露出部分14を有する細孔は、選択(間引き)されたものであり、このように選択(間引き)された細孔を用いることにより、細孔密度を制御した多孔質層を提供できるようになる。

【0030】図6 (b) は、図6 (a) で選択(間引き)された細孔に充填材料15を充填した後の工程断面図を示す。選択(間引き)された細孔に充填材料15を充填する方法は、電気化学的堆積、即ち、電気メッキが好ましい。図6 (b) のように、充填材料15は、電気メッキにより、シリコン基板11が露出した細孔に選択的に充填され、結果的に第1の細孔群の細孔が間引きされた。このように、本願発明の多孔質層は、アルミニウム基板だけではなく、シリコン基板、ガラス基板上にも形成可能であり、電子デバイス、光デバイス等の種々のデバイスに搭載可能であることが確認できた。

【0031】<第3の実施形態>本実施形態では、第2の実施形態と同様に、シリコン基板等の支持基板11を用いた場合の多孔質層の製造方法を図7を用いて説明する。本実施形態に於いては、真空マイクロデバイスを代表例に挙げて説明する。特に、低電圧駆動可能な電子源の製造方法の一例として、カーボンナノチューブ電子源の製造方法を説明する。但し、本願発明の電子源材料としては、このような炭素材料に限定され得るものではない。

【0032】図7 (a) は、図6 (a) と同様にして2段階陽極酸化法で支持基板11上に細孔構造を形成し、その細孔構造を鋳型としてカーボンナノチューブ16を形成した後の工程断面図を示す。カーボンナノチューブ16は、CVD (Chemical Vapor Deposition) 法で形成され得るものである。このようなカーボンナノチューブ16の形成方法としては、第2の細孔群の細孔4の底部の支持基板露出部14に金属触媒を配設し、この金属触媒を成長起点として、カーボンナノチューブを形成する方法 (特許第3008852号のカーボンナノチューブ形成方法を参照) もある。図7 (a) のように、カーボンナノチューブ16は、第1の細孔群の細孔3、及び第1の細孔群の細孔3と第2の細孔群の細孔4が接続して形成した貫通細孔のそれぞれに形成された。

【0033】図7 (b) は、選択 (間引き) された細孔の先端を露出した後の工程断面図を示す。陽極酸化膜2からのカーボンナノチューブ16の先端露出は、ウエットエッティング法を用いた。陽極酸化膜2除去のためのエッティングとしては、フッ酸、リン酸、水酸化ナトリウム、リン酸／塩酸等が用いられる。このようなウエットエッティングを行うと、図7 (b) のように、第1の細孔群の細孔3と第2の細孔群の細孔4が接続して形成した貫通細孔以外の細孔3に形成したカーボンナノチューブ16aは、陽極酸化膜2のエッティングと共に、リフトオフされ、貫通細孔に形成したカーボンナノチューブ16のみが残存する。結果的に、形成するカーボンナノチューブ16は間引きされ、カーボンナノチューブ16の密度は減少する。

【0034】但し、図7 (a) で説明した細孔構造を鋳型とするCVD法によるカーボンナノチューブの製造方法の場合、細孔3及び4の内壁だけではなく、陽極酸化膜2表面に対しても炭素膜が被覆されるため、陽極酸化膜2表面の炭素膜を除去する必要がある。陽極酸化膜2表面の炭素膜は、RIE (Reactive Ion Etching) を用いた酸素プラズマエッティングで容易に除去可能である。以上のように、2段階陽極酸化法を用いることにより、カーボンナノチューブの密度が低減し、カーボンナノチューブの先端を露出することにより、電界集中を高め、低電圧エミッションを可能にすることことができた。

【0035】<第4の実施形態>第4の実施形態に於いては、別の2段階陽極酸化法を用いた多孔質層の製造方法を説明する。第1の実施形態と異なる点は、第1段階目の陽極酸化 (第1の細孔群) の化成電圧に対して、第2段階目の陽極酸化 (第2の細孔群) の化成電圧を減少することにより、選択 (間引き) した細孔構造の細孔を有する多孔質層を製造する。図8～9は、本実施形態の多孔質層の製造方法を示す工程断面図である。

【0036】図8は、図1と同様に、アルミニウム基板

1に対して、第1段階目の陽極酸化を行った後の工程断面図を示す。陽極酸化条件は、0.3M シュウ酸、温度：16℃、印加電圧：40V であった。図8のように、アルミニウム基板1上に陽極酸化膜2が形成すると共に、第1の細孔群の細孔3が形成した。図9は、第2段階目の陽極酸化を行った後の工程断面図を示す。陽極酸化条件は、0.3M シュウ酸、温度：16℃、印加電圧：20V であり、第1の細孔群の細孔3aを間引きした第2の細孔群の細孔 (細孔集合体) 17が形成した。

【0037】この時、選択率 (間引き率) K (第1の細孔群の細孔のピッチ18/第2の細孔群の細孔集合体が形成した細孔のピッチ19) は、第1段階目 (第1の細孔群) の陽極酸化の印加電圧：V1、第2段階目 (第2の細孔群) の陽極酸化の印加電圧：V2を用い、  
 $K = V2/V1$

となり、本実施形態に於いては、1/2となる。即ち、第1の細孔群の細孔の2つに1つが第2の細孔群の細孔 (細孔集合体) 17が形成する。この時、陽極酸化膜2を貫通する細孔の細孔密度は、第1の細孔群の細孔の1/4に減少した。

【0038】以上のように、第1の実施形態と同様に、第1段階目 (第1の細孔群) の陽極酸化の印加電圧、第2段階目 (第2の細孔群) の陽極酸化の印加電圧を制御することにより、デバイス設計に応じて選択 (間引き) された第1の細孔群の細孔に第2の細孔群の細孔 (細孔集合体) が設けられ、陽極酸化膜2の一方の表面からもう一方の表面へ貫通する貫通細孔の密度が制御可能になった。

【0039】次に、このような構成の多孔質層をデバイスに応用するための代表例を図10、図11で説明する。図10 (a)～(c) は、アルミニウム基板を用いた場合の代表例 (化学センサーに応用可能な構成) であり、図11 (a)～(c) は、ガラス基板、シリコン基板等の支持基板11を用いた場合の代表例 (電子源に応用可能な構成) である。

【0040】図10 (a) は、図9で示した多孔質層に於いて、アルミニウム基板1を除去し、電極20を設けた後の工程断面図を示す。アルミニウム基板1は、リン酸／硝酸／酢酸の混酸でエッティング除去した。電極20は、スパッタ法、蒸着法で堆積した。図10 (b) は、第2の細孔群の細孔集合体17のバリア層を除去後、間引きされた細孔にセンシング材料22を充填した後の工程断面図を示す。バリア層はフッ酸で除去し、細孔集合体17に開口部21を設けた。図10 (c) は、充填したセンシング材料22の先端を露出した後の工程断面図を示す。陽極酸化膜2は、ウエットエッティング法、または、化学的・機械的研磨法を用いて除去した。陽極酸化膜2を除去することにより、第2の細孔群の細孔集合体が形成した第1の細孔群の細孔にのみ充填されたセンシング材料22の先端が露出した。

【0041】次に、もう一つのデバイスの応用例を説明する。図11(a)は、第2の実施形態で説明したように、シリコン基板11上にアルミニウム堆積膜2を形成し、図8及び図9のようすに第1及び第2段階目の陽極酸化を施し、CVD法で炭素膜16を細孔3、17の内壁に被着した後の工程断面図を示す。アルミニウム堆積膜2は、シリコン基板11上にスパッタ法で2μm形成した。また、第1段階目の陽極酸化は0.3Mシュウ酸中(温度:16℃)、40Vで行い、第2段階目の陽極酸化は0.3Mシュウ酸中(温度:16℃)、20Vで行った。炭素膜(カーボンナノチューブ)は、石英反応管中、800℃、プロピレン(窒素中2.5%)を3時間流通させることで形成した。

【0042】図11(b)は、カーボンナノチューブ16を空間に露出した後の工程断面図である。陽極酸化膜2をフッ酸等でエッティング除去することにより、カーボンナノチューブの先端が露出する。この時、露出したカーボンナノチューブは、第1の細孔群の細孔3と第2の細孔群の細孔集合体17からなる貫通細孔に形成するカーボンナノチューブ23、及び第1の細孔群単独の細孔に形成されるカーボンナノチューブ24とからなるものの、カーボンナノチューブ24は電気的にフローティングしているため、実質的にカーボンナノチューブ23のみがデバイス的に活性である。従って、結果的に第1段階目の陽極酸化で形成した細孔は間引きされ、細孔密度(カーボンナノチューブ密度)は低減された。但し、カーボンナノチューブ24がデバイス構造的に問題がある場合、陽極酸化膜2のオーバーエッティングにより、リフトオフし、不要なカーボンナノチューブ24を除去することが必要である。

【0043】以上のように、2段階陽極酸化法を用い、第2段階目の陽極酸化の化成電圧を第1段階目の陽極酸化の化成電圧よりも小さくすることにより、第1段階目の陽極酸化で形成した細孔が間引きされ、実質的に形成するカーボンナノチューブ電子源の密度が低減されることにより、電界集中が高められ、低電圧エミッションが可能な電子源が提供できた。

#### 【0044】

【発明の効果】以上のように、本願発明の多孔質層は、ナノ構造を有する第1の細孔群を所望の間隔で間引きすることによって得られるため、簡単な構造を有する多孔質層でありながら、所望の制御された細孔密度のものを容易に得ることができる。また、本願発明による多孔質層の製造方法は、多段階陽極酸化に於ける化成電圧を変化させることに基づくため、大面積な多孔質層の形成を可能とし、同時に、微細加工可能な、高価な製造装置が一切不要となった。更に、本願発明による多孔質層は、低密度のナノ構造体を有するデバイスに有利な構造を提供するものであり、特に、化学センサー、電子源のデバイス特性向上を可能にした。

#### 【図面の簡単な説明】

【図1】第1の実施形態に於ける多孔質層の工程断面図を示す。

【図2】第1の実施形態に於ける多孔質層の工程断面図を示す。

【図3】第1の実施形態に於ける多孔質層の工程断面図を示す。

【図4】第1の実施形態に於ける多孔質層を用いた化学センサーの工程断面図を示す。

10 【図5】第2の実施形態に於ける多孔質層を用いた電子デバイスの工程断面図を示す。

【図6】第2の実施形態に於ける多孔質層を用いた電子デバイスの工程断面図を示す。

【図7】第3の実施形態に於ける多孔質層を用いたカーボンナノチューブ電子源の工程断面図を示す。

【図8】第4の実施形態に於ける多孔質層の工程断面図を示す。

【図9】第4の実施形態に於ける多孔質層の工程断面図を示す。

20 【図10】第4の実施形態に於ける多孔質層を用いた化学センサーの工程断面図を示す。

【図11】第4の実施形態に於ける多孔質層を用いたカーボンナノチューブ電子源の工程断面図を示す。

【図12】アルミナ陽極酸化膜の斜視図を示す。

#### 【符号の説明】

1 アルミニウム基板

2 陽極酸化膜

3、3a 第1の細孔群の細孔

4 第2の細孔群の細孔

30 5 第1の細孔群の細孔のピッチ

6 第2の細孔群の細孔のピッチ

7 微細孔

8 電極

9 第2の細孔群の細孔底部の開口部

10 センシング材料

11 支持基板

12 アルミニウム堆積膜

13 第2の細孔群の細孔のバリア層

14 第2の細孔群の細孔底部のコンタクト部

40 15 充填材料

16 カーボンナノチューブ

17 細孔集合体

18 第1の細孔群の細孔のピッチ

19 第2の細孔群の細孔集合体が形成した第1の細孔群の細孔のピッチ

20 電極

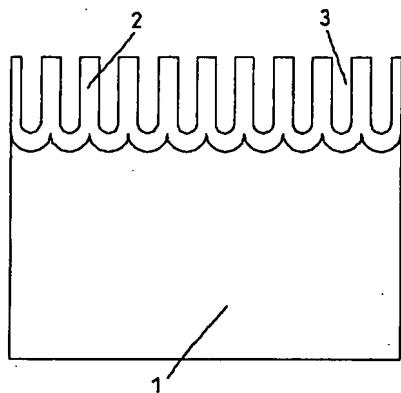
21 細孔集合体底部の開口部

22 センシング材料

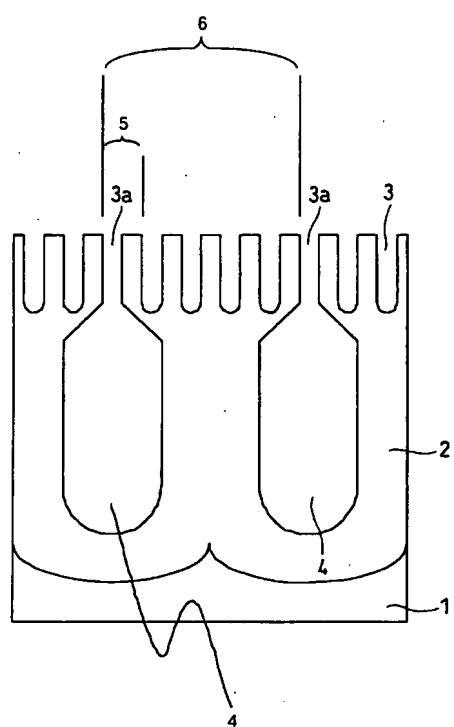
23 下地層とコンタクトしたカーボンナノチューブ

50 24 フローティングしたカーボンナノチューブ

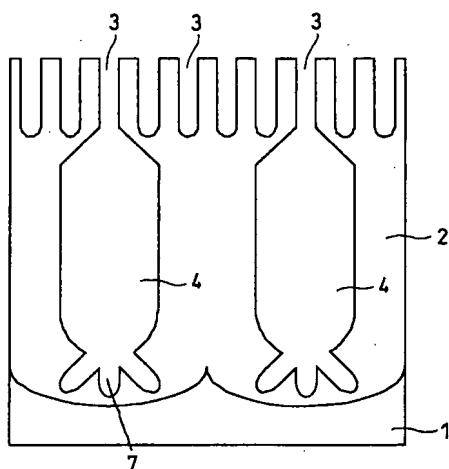
【図1】



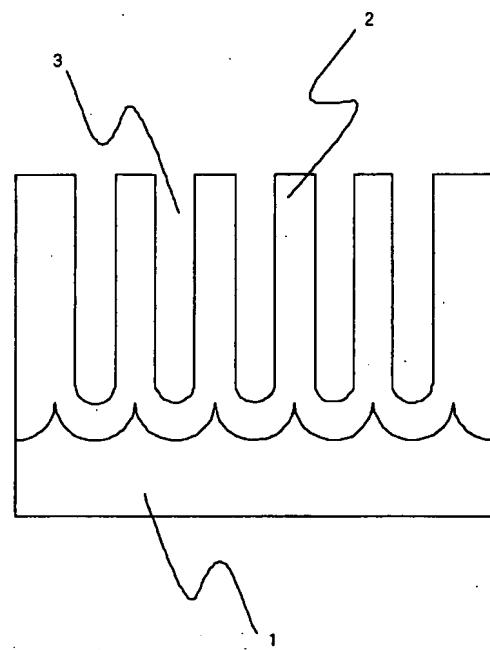
【図2】



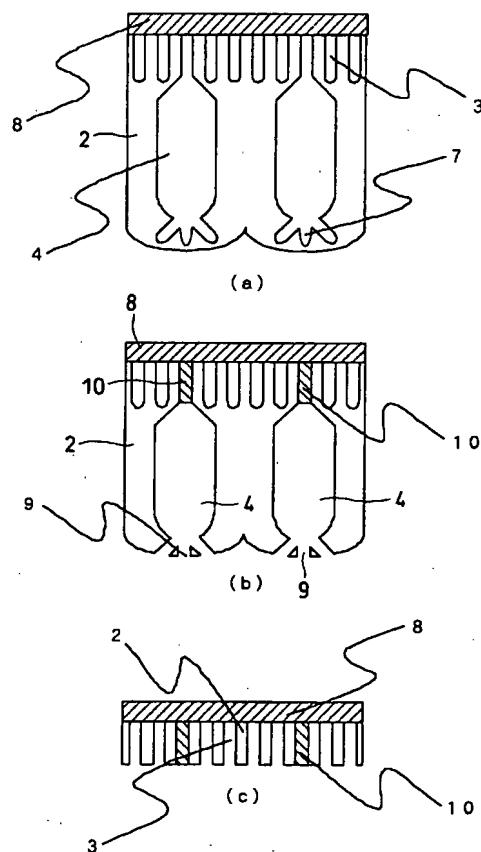
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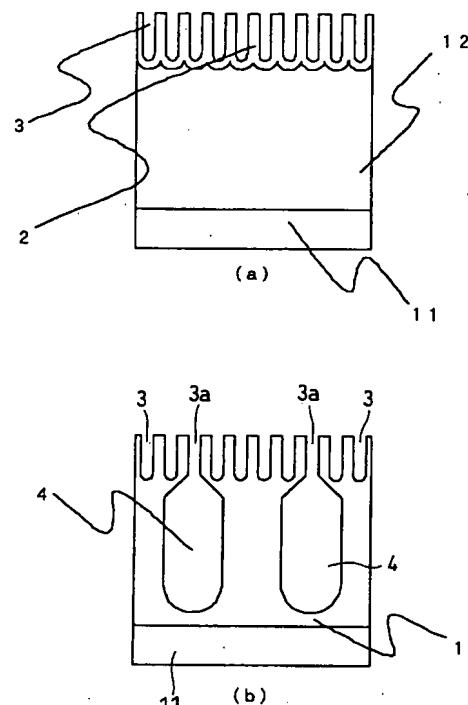
【図8】



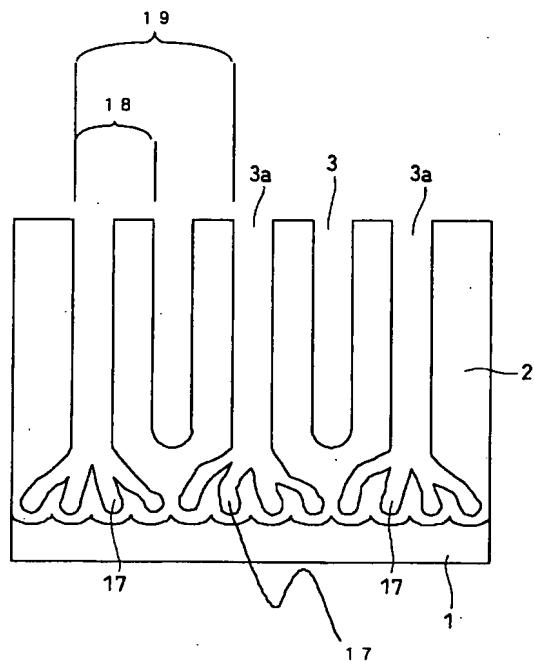
【図4】



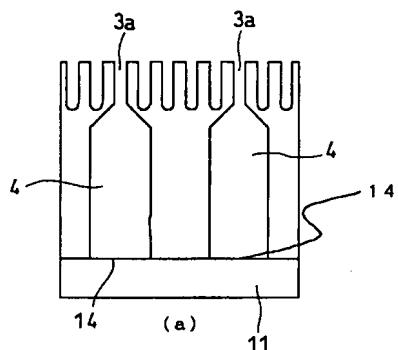
【図5】



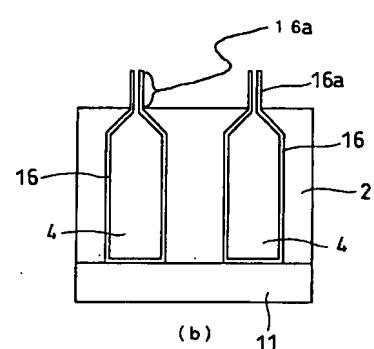
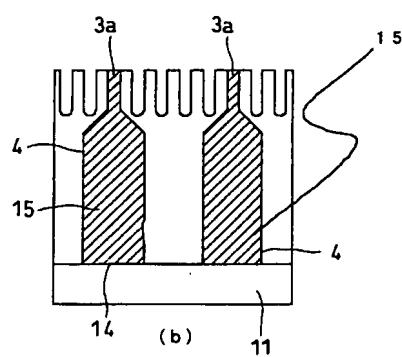
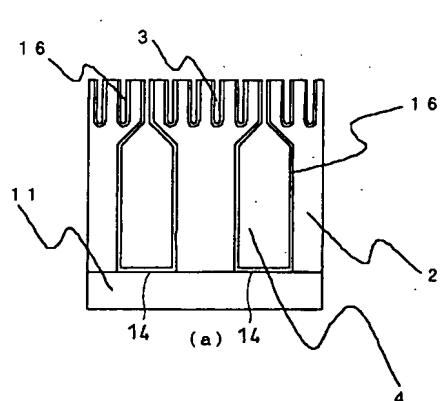
【図9】



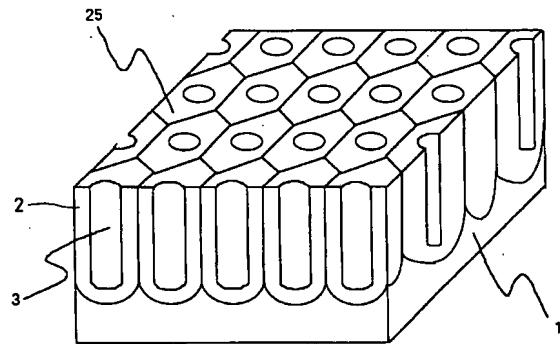
【図6】



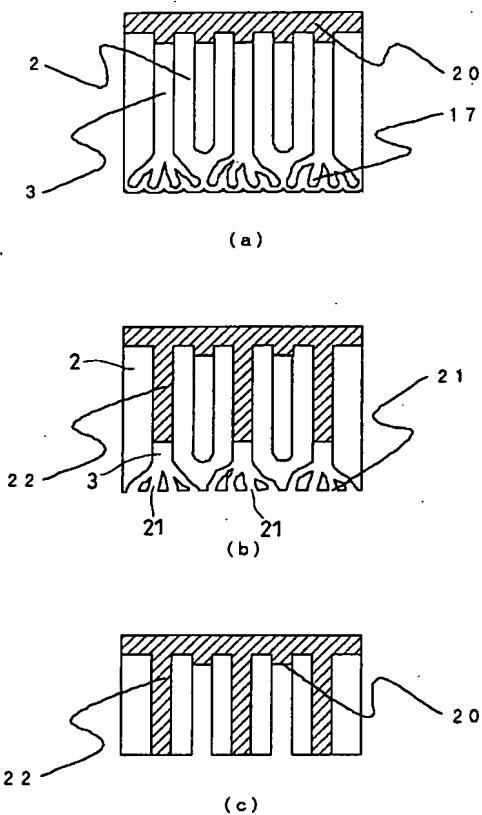
【図7】



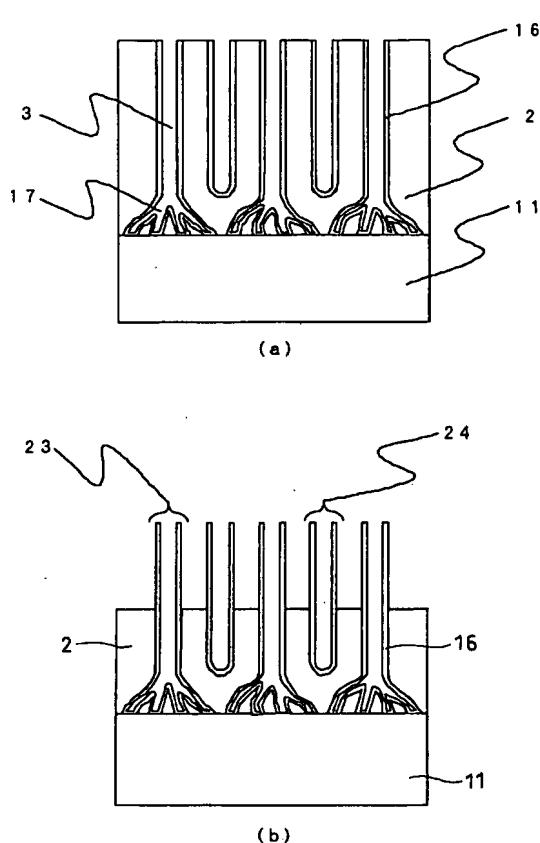
【図12】



【図10】



【図11】



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